TECHNICAL REPORT

TWIN BUTTE

SOILS AND WATER EVALUATION

TASK FORCE

AUGUST, 1984

August 3, 1984

HON. FRED BRADLEY
Minister of the Environment
Legislative Buildings
Edmonton, Alberta

Mr. Minister:

We take pleasure in submitting the TECHNICAL REPORT of the TWIN BUTTE SOILS & WATER EVALUATION TASK FORCE. We have also attached an Executive Summary and the technical appendices to this report in separate volumes for future reference.

Respectfully,

Hilton R. Pharis,
Chairman

Dr. Eric Tollefson

Ron Zukiwsky

Dr. Tadeusz Dabrowski

Bob Clark

Dr. John Ashworth

Wendy Carpentier

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A-2 Additional Test Data, W.T. Tanguay, Metro Tech Systems Ltd.

A-3 Wind Speed and Direction.

A-4 Composition of Condensate from Shell Waterton Field.

Volume II - Appendices Relative to Hydrology

H-1 Evaluation of the Surficial Geology, Hydrogeology and Water Quality Survey at Shell Canada Resources Limited, Waterton Gas Plant, May 1984.

H-2 Evaluation of the Surficial Geology, Hydrogeology and Water Quality Survey at Gulf Canada Resources Inc., Pincher Creek Gas Plant, May 1984.

H-3 Hydrochemistry of the Twin Butte Area, Alberta: Evaluation of the Potential for Degradation of Water Quality Due to Sour Gas Plant Operations, E.I. Wallick, Alberta Research Council, June 1984.

H-4 Tap Water Sampling Program for Trace Elements, Twin Butte Area, Energy Resources Conservation Board, May 1984.

H-5 Miscellaneous Surface Water and Groundwater Analyses, May 1984.

Volume III - Appendices Relative to Soils and Vegetation

S-1 Descriptions of Methods of Collection and Discussion of Results of Analyzing Samples of Soil, Surface Litter, Vegetation, Pond Water and Lake Sediment Taken in the Twin Butte Area. Hardy & Associates, Norwest Labs, Saskatchewan Research Council.

S-2 Analyzing Sulphur Isotope Samples of Soil, Surface Litter, Vegetation, Lake Sediments etc. Taken in the Twin Butte Area.

S-3 Location and Results of Analyzing Samples of Vegetables Grown in the Twin Butte Area for Metals.

CHAPTER ONE

INTRODUCTION

The Twin Butte Soils and Water Evaluation Task Force was appointed by Ministerial Order of the Hon. Fred Bradley, Minister of Environment on April 28, 1983. The Task Force was made up of the following members:

- Mr. Hilton Pharis, Chairman;
  A rancher and Reeve of the Municipal District of Pincher Creek.

- Mr. Ron Zukiwsky;
  School Principal and Pincher Creek Town councillor.

- Mr. Bob Clark;
  Former member of the Legislature for Olds-Didsbury.

- Mrs. Wendy Carpentier;
  An area resident and President of the Pincher Creek Industrial Pollution Committee.

- Dr. Eric Tollefson;
  Professor of Chemical Engineering, University of Calgary.

- Dr. Tadeusz Dabrowski;
  A Calgary hydrogeologist with the firm of Piteau and Associates.

- Dr. John Ashworth;
  A soil chemist with Norwest Soil Research Ltd. in Edmonton.

The Terms of Reference of the Task Force as outlined by the Minister of Environment were:

1. determine the nature and level of substances which are contained on the Gulf Pincher Creek and Shell Waterton gas plant sites resulting from the gas plant operations;
2. determine if any surface or sub-surface migration of these substances off of the plant site areas has occurred and the extent thereof.

The Task Force was also directed to conduct an independent study to evaluate the Gulf Canada report which identified heavy metals and organic compounds on the Gulf site.

The study area included:

- the populated areas immediately surrounding the Shell Waterton and Gulf Pincher Creek Plants
- the rural areas of Glenwood, Hill Spring and Twin Butte.

The objectives of the Task Force were established through a series of meetings with concerned citizens, visits to the plant sites and reviews of the existing reports regarding the soil and water on both plant sites. Following this process, the committee developed and conducted a research program that met the Terms of Reference set out for the Task Force.

Surface migration was discussed at length by the committee and taken to include the gaseous particulate emissions leaving the incinerator and flare stacks of the plants as well as particulate and gaseous matter carried by the wind from above the plant site. The Minister of Environment was advised and agreed with the intentions of the Task Force to include this concern in its mandate.

The Task Force outlined a program to be conducted by consulting and research organizations, coordinated its execution and evaluated the results. This program included:

- Hydrochemical Study of the Twin Butte area by Alberta Research Council.

- Source and Ambient Air Evaluation Study for the Twin Butte area by the Kananaskis Centre for Environmental Research.

- Pincher Creek Trace Element Study by Hardy Associates (1978) Ltd.

Several analytical projects of a less extensive nature designed to determine the quality of specific aspects of soil, air and water were undertaken by:

Saskatchewan Research Council
Chemex
University of Calgary, Physics Department
University of Windsor, Chemical Engineering Department
Metro Tech Systems Ltd.
Alberta Research Council
Chemical and Geological Lab
Others

The work of the Task Force is documented in this Executive Summary, a more detailed Technical Report and three separate volumes of Technical Appendices. These documents were prepared by the Task Force Members and were then reviewed and approved by the Task Force as a whole before publication. The Task Force expresses its appreciation to Executive Suite Business Centres Ltd. for editorial and word processing assistance provided during the preparation of the several draft and final documents.

CHAPTER TWO

TASK FORCE ACTIVITIES

From May 9, 1983 to July 5, 1984 the Twin Butte Soils and Water Evaluation Task Force held 21 regular meetings, involving presentations and delegations from scientists, industry people, and local individuals and groups having an interest in the study.

Several tours of the Gulf Pincher Creek and Shell Waterton plant sites were taken by the Task Force as a group. In addition, periodic visits throughout the study were made to the plants by one or more of the members of the Task Force for general observation and for supervision of the research and study efforts by the Task Force and its consultants.

Two public meetings were held in Pincher Creek to provide information and opportunities for input to those residents who were interested in the Task Force activities.

The public and regular meetings of the Task Force are outlined below in chronological order indicating their location and any delegations or technical presentations that occurred. Many additional meetings occurred among sub groups of members of the Task Force during the course of our activities.

1. May 9, 1983, Pincher Creek
   - Initial organizational meeting and tour of gas plants by Task Force members.

2. May 27, 1983, Pincher Creek
   - Delegation from Pincher Creek Area Environmental Association - Don Taylor, Dianne McGlynn, Glen Barfuss, Sophie Taylor, Agnes Heppner, R. Furlong.
   - Presentation by Gulf and Monenco - Vern Mumby, Martyn Riddle, Thom Kewen, Alex Shumacher.
   - Update report from Alberta's Energy Resources Conservaton Board (ERCB) by Ed Brushett.

3. June 16, 1983, Calgary
   - Presentation of his report on the Twin Butte Environmental Health Study - First Report, by Dr. Earle Snider of University of Alberta
   - Presentation by Shell - Art Mathes and C. Paulsen.

- Report on University of Windsor Study on Trace Element Emissions from Stacks of Sour Gas Plants by Dr. Harald Thimm of the ERCB.

4. July 5, 1983, Pincher Creek
   - Presentation of his findings on the Sage Institute's Report, "Pincher Creek Health Study", by Dr. B. Stringham.

5. August 8, 1983, Calgary
   - Update report of ERCB findings by Vern Millard and Dr. Harald Thimm.

6. August 16, 1983, Calgary
   - Presentations of proposed research programs by Dr. Ed Wallick, and Mr. Gordon Gabert of the Alberta Research Council on chemical weathering; by Dr. Harald Thimm on the ERCB sampling program and by Mr. R. Leitch of Hardy and Associates on soils, vegetation and lake sediment sampling programs.

7. September 14, 1983, Pincher Creek
   - Presentations to the Task Force by Bob Lyons, Dr. Charles Zachar and Barbara Olson.
   - Public meeting to outline Task Force proposed activities. Approximately 30 people in attendance.

8. September 15, 1983, Pincher Creek
   - Delegation of local residents, Lester Hochstein and Art Bonertz.

- Letter from Dorothy Blackburn.
- Update report by Gulf - Lin Callow, George Campbell, Brian Plesuk, Vern Mumby and Liz Maurice.
- Delegation from Pincher Creek Area Environmental Association - Sophie Taylor.

9. October 20, 1983, Pincher Creek
   - Report by Mr. Mel Strosher of the Kananaskis Research Centre on Twin Butte Ambient Air Study.

10. December 8, 1983, Pincher Creek
   - Update report by Gulf - Vern Mumby, George Campbell, Brian Plesuk, Lin Callow.
   - Presentation by Dr. E. Wallick and Mr. T. Balakrishna on research on Chemical Weathering.
   - Update report from ERCB by Dr. Harald Thimm.

11. January 10, 1984, Pincher Creek
   - No delegations or presentations.
   - Letter from Frank Bishop, Fish and Wildlife Division, E.N.R., Lethbridge.
   - Internal review and discussion of research data.

12. January 26, 1984, Calgary
   - Presentations by Mr. Mel Strosher of the Kananaskis Research Centre on gaseous and particulate emissions from the stacks; by Dr. Mike Prior, Alberta Environmental Centre on their research into selenium deficiency and into the

effects of SO_2 on animal health, and by Dr. B. Church, of the University of Calgary on the effects of sour-gas plants on ranching operations.

13. March 5, 1984, Pincher Creek
    - Progress review and discussion of analysis and research programs.

14. April 9, 1984, Pincher Creek
    - Progress review and discussion of analysis and research programs.

15. April 30, 1984, Calgary
    - Progress review and discussion of analysis and research programs.

16. May 1, 1984, Calgary
    - Progress review and discussion of analysis and research programs.

17. May 24, 1984, Pincher Creek
    - Public meeting to discuss results of sampling program with participants.

18. May 25, 1984, Pincher Creek
    - Discussion regarding editorial and word processing services with Mr. Norm Duce of Executive Suite Business Centres Ltd.

19. June 18, 1984, Lethbridge
    - Review of first draft of Technical Report.

20. July 11, 1984, Lethbridge
    - Review of second draft of Technical Report and Executive Summary.

21. August 2, 1984, Lethbridge
    - Review of third draft of Technical Report and Executive Summary.

CHAPTER THREE

SURFACE WATER AND GROUNDWATER HYDROLOGY

This chapter outlines the background, the study objectives and our findings and conclusions regarding Geology, Surface Water and Hydrogeology in the Twin Butte area.

BACKGROUND

In September 1982, Gulf Canada Resources Inc. commissioned Monenco Consultants Limited to conduct a reconnaissance field sampling program at Pincher Creek Gas Plant to:

1) determine the spatial extent, type and level of contamination,
2) define the criteria for clean-up and reclamation requirements,
3) suggest possible clean-up and reclamation options.

The reconnaissance field program completed by Monenco in November 1982 identified several toxic metals in high concentrations in wastewater and surface runoff collection ponds and high levels of sulphates in groundwater in the sulphur block area. The results of this study raised the concerns of the local residents regarding potential health hazards related to the potential surface and groundwater contamination resulting from the operation of the plant.

Following this discovery in December 1982, Alberta Social Services and Community Health initiated the Twin Butte Environmental Health Study. A study conducted by E. L. Snider (1983) indicated that the health problems reported from the area might be related to the deficiency of some elements (calcium, magnesium, selenium) and higher levels of toxic metals (mercury, cadmium), which were determined based on hair chemical analyses. This study included a limited survey of the water supply sources.

Considering that water can be easily contaminated as a result of industrial activities, the Minister of Environment appointed the Twin Butte Soils and Water Evaluation Task Force in April 1983. One of the Task Force objectives was determination of the potential surface water and groundwater contamination due to Gulf Pincher Creek and Shell Waterton gas plant operations.

Study Objectives

The general objective of the study was to determine if the surface water and groundwater quality in the Twin Butte area had been affected by the Gulf Pincher Creek and Shell

Waterton sour gas plant operations.

The specific objectives of this study were as follows:

1) determine the quality of water retained in the ponds and basins within gas plant boundaries and evaluate the potential for surface water contamination due to effluent discharge;

2) determine the groundwater quality within gas plant boundaries and define the potential for groundwater contamination as a result of plant operations;

3) establish surface water and groundwater quality in the area potentially affected by the plant operations and in the control areas;

4) determine the relationship between surface water and groundwater in the study area;

5) assess the geochemical effects of SO_2 emissions on the Quaternary sediments (soil and till) with respect to the evolution of major constituents and the release of heavy metals;

6) evaluate the potential of using the chemical composition of atmospheric moisture to determine whether the levels of SO_4 present showed any relation to gas plant emissions;

7) evaluate Gulf Canada Reports related to the Pincher Creek Gas Plant Reclamation Planning.

Work Plan

To address the water quality concerns in the Twin Butte area, an exploration program for the Task Force study was developed. It included the following tasks:

1) Reviewing the hydrological and geological literature.

2) Collecting and reviewing all the available water quality data for the study area.

3) Reviewing the results of geological, geotechnical and hydrological studies conducted within the Shell and Gulf plants.

4) Developing an exploration program based on the literature and water quality data review. This program was developed in cooperation with and included the suggestions of individuals and representatives of local residents regarding sampling point locations.

5) Initiating and conducting an exploration program required for assessing the existing water quality data and defining the impact of the gas plants on water quality.

The work required for the first three tasks was conducted by the Task Force members. Task 4 was developed jointly between the Task Force, Dr. E. I. Wallick (Alberta Research

Council) and local residents (suggestions regarding water sampling locations). Task 5 was carried out by the Alberta Research Council in close cooperation with the members of the Task Force.

The exploration program developed by the Task Force concentrated on inorganic compounds of water with a special emphasis on heavy metals. The results of analyzing shallow groundwater, from sites on or near both gas plants, for organic chemicals were also considered.

Five potential sources of surface water and groundwater contamination were considered. These were:

- accidental spills of contaminants on the site,
- seepage from process basins and surface runoff ponds,
- leachate movement from the landfill sites,
- effluent disposal,
- precipitation of gaseous emissions from the incinerator and flare stacks and sulphur dust deposition on the ground surface.

It was also recognized that organic compounds from the incinerator and flare stacks could contribute to water contamination. Rather than analyze each water sample for hundreds of possible organic components, it was decided to conduct a survey of components leaving the plants via the air mass. Now that it has been shown that there are organic compounds of concern in the air (Strosher, 1982 and 1984), an additional water sampling program is being recommended.

Sources of Information

The regional publications on hydrology, geology and groundwater were reviewed. When used as a reference in the report, they are listed in the bibliography. A number of unpublished reports, prepared by the government agencies and consultants contracted by the Gulf and Shell plants were utilized in the Task Force study. References are included in the appendices, which have been considered as a data source for the study.

The water quality data and geological logs (if available) were obtained from Alberta Environment, Groundwater Resources Information Service, Earth Sciences Division.

DESCRIPTION OF THE AREA

Information concerning location and topography, climate, surface hydrology, geology, and hydrogeology are summarized in the following sections as background to the study.

Location and Topography

The study area is located in the southern part of the Municipal District of Pincher Creek (No. 9). It includes:

Township 3, Ranges 28, 29 and 30 West of 4 Meridian
Township 4, Ranges 28, 29 and 30 West of 4 Meridian and Range 1 West of 5 Meridian
Township 5, Ranges 28, 29, and 30 West of 4 Meridian and Range 1 West of 5 Meridian.

Additional samples were collected from the Hill Spring and Glenwood area (Municipal District of Cardston, No. 6).

Locations of the surface and groundwater sampling points are shown in Figure III-1.

The Twin Butte area is located in the Rocky Mountain foothills on the eastern periphery of the Clark Range of the Western Cordillera. Local relief in the foothills varies from about 1180 m to about 1500 m. The Clark Range, approximately 4 km west of the Shell site, presents very strong relief. Elevations vary from about 2450 m at the peaks to about 1500 m in the valleys.

In contrast, the foothills area has a gently rolling hilly landscape of comparatively subdued relief. Further east, the topography becomes progressively more subdued, eventually becoming gently undulating with elevations varying from about 1180 m to about 1100 m.

Climate

The climate of the area is humid continental and is characterized by long, cool summers.

January is the coldest month with a mean temperature of -10.2°C (Pincher Creek Town - Environment Canada, 1982a). July is the warmest month with a mean temperature of 16.5°C. The mean annual temperature at the Town of Pincher Creek is 4.1°C.

The mean annual precipitation at Pincher Creek Town is 589.2 mm (Environment Canada, 1982b). However, the total precipitation increases substantially towards the mountains. For example, Waterton Park Headquarters, some 50 kilometers

distant, records a mean annual precipitation of 1072 mm. The mean annual precipitation at the plant sites is about 780 mm (Tokarsky, 1974).

Potential evapotranspiration for the general area is about 400 mm per annum (Hydrological Atlas of Canada).

The mean wind speed is approximately 20 km/hr and the prevailing direction is from the west (Pincher Creek - Environment Canada, 1982c). The percentage frequency of the wind directions in the area are plotted as a rose diagram (Fig. III-2). This diagram clearly shows the predominant nature of winds from the west in the Pincher Creek area. A particular feature of the foothills is the Chinook wind. This wind represents periodic incursions of comparatively warm Pacific air moving eastward over the Cordillera. Their effect is especially pronounced in the winter when they can cause appreciable melting of the snow within short time periods.

It should be noted that the percentage frequency of the wind directions measured at the Pincher Creek airport may not be representative for the Twin Butte area. In this area, the wind directions will be locally affected by the terrain topography expressed by the hill ridges and deeply incised valleys. Data for Pincher Creek airport were used in this study, because it is the closest climatological station to the study area having complete wind measurements.

BEAUVAIS LAKE PROV. PARK

R. 30

6

R. 29

R. 28

R. 27

507

Tp. 5

FIFTH MERIDIAN

2ND BASE LINE

Prairie Bluff

SHELL WATERTON GAS PLANT
FOR LOCATION OF SAMPLING POINTS SEE FIG. III-1

Tp. 4

Victoria Peak

Tp. 3

505

810

800

Glenwood

Hartleyville

Irrigation

GULF PINCHER GAS PLANT
FOR LOCATION OF SAMPLING POINTS SEE FIGS. III-1 & III-3

Twin Butte

Waterton Reservoir

Belly R.

Waterton

NOTES:

1. LOCATION OF SAMPLING POINTS IS ACCURATE WITHIN A QUARTER SECTION.
2. THE NUMBER OF GROUNDWATER SAMPLING POINTS INDICATED ON THE MAP MAY EXCEED THE NUMBER OF WELLS ACTUALLY DRILLED. IT WAS NOT POSSIBLE TO ESTABLISH, BASED ON SAMPLING RECORDS, WHETHER ONE WELL WAS SAMPLED A NUMBER OF TIMES OR WHETHER A NUMBER OF WELLS WERE DRILLED WITHIN THE SAME QUARTER SECTION.

LEGEND

SURFACE WATER SAMPLING POINT ●

GROUNDWATER SAMPLING POINT (WELL/SPRING) ▲

1000 0 1000 2000 3000 4000m

SCALE 1:125,000

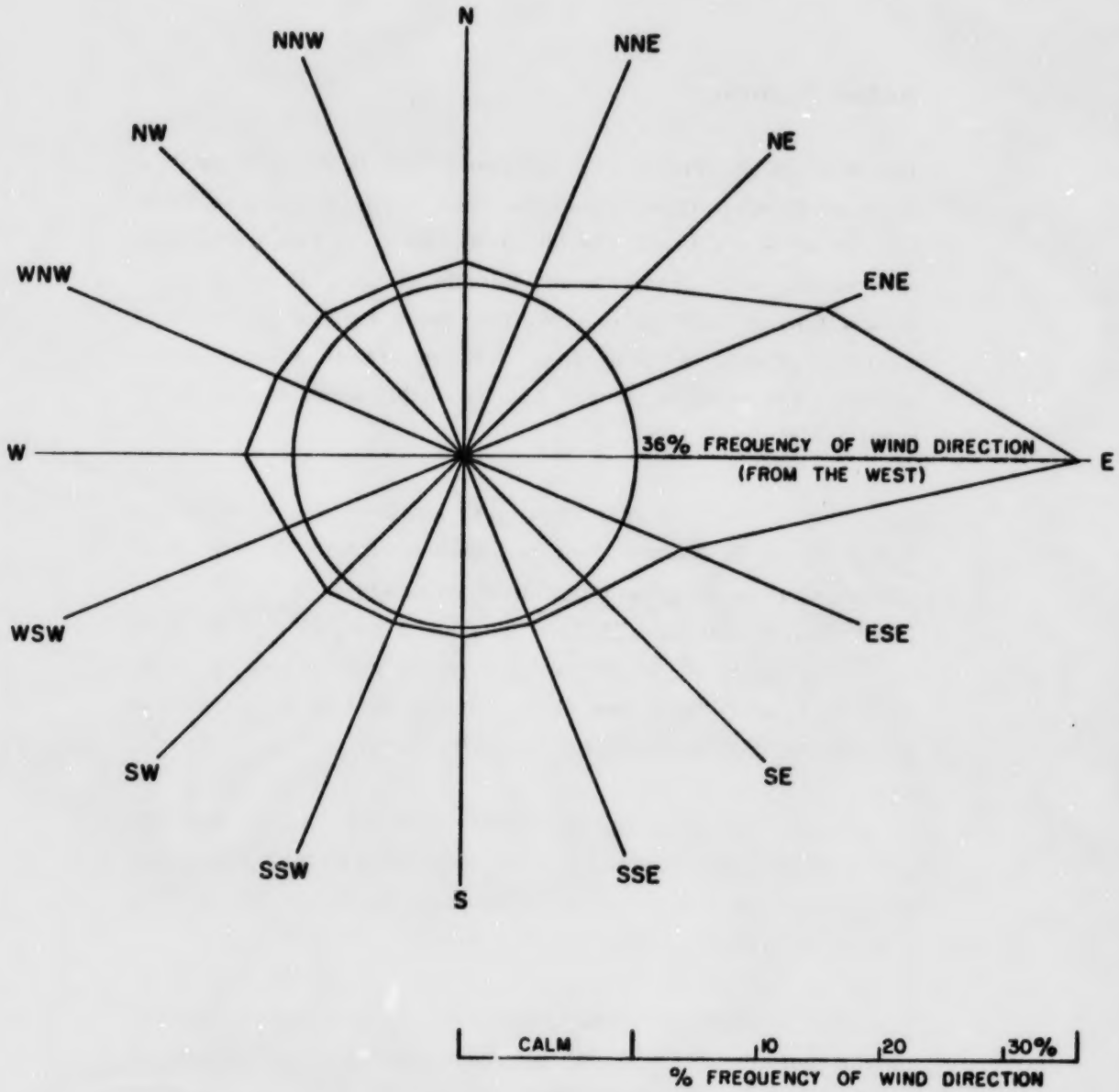
TWIN BUTTE SOIL AND WATER TASK FORCE

TWIN BUTTE AREA GROUNDWATER AND SURFACE WATER SAMPLING LOCATIONS

DATE JUNE, 1984

DRAWN BY S. ELLERT

FIGURE NO. III-1



SCALE: 20mm = 10% FREQUENCY OF WIND DIRECTION

TWIN BUTTE SOIL AND WATER TASK FORCE	
PERCENTAGE FREQUENCY OF WIND DIRECTION DEPICTED AS A ROSE DIAGRAM PINCHER CREEK AIRPORT	
DATE JUNE, 1984	FIGURE NO. III - 2
DRAWN BY S. ELLERT	

Surface Hydrology

The area in the vicinity of the two plants is drained by the Drywood Creek. Upstream of the Shell plant (gauging location LAT 49 18 00 N, LONG 114 00 20 W) the river has a drainage area of 29.3 km^2 (Environment Canada, 1983). It has a mean annual flow of 0.967 m^3/s. Monthly mean discharges reach a maximum of 2.61 m^3/s in June. Flows are at a minimum in winter. For example, March has a monthly mean discharge of 0.121 m^3/s.

Upstream of the Gulf plant (gauging location LAT 49 17 38 N, LONG 113 47 35 W) the river is joined by South Drywood and Yarrow Creeks to give a combined drainage area of 238 km^2 (Environment Canada, 1983). The mean annual flow is 2.99 m^3/s. Monthly mean discharges reach a maximum of 13.8 m^3/s in June. Flows are at a minimum in February, with a monthly mean discharge of 0.546 m^3/s.

In general, however, the land surface in the vicinity of both plants is not well drained. Numerous intermittent lakes and sloughs are present. This is at least partially due to the hummocky nature of the moraine deposits.

A number of chemical surveys of surface waters were conducted in the period 1971 - 1984 to assess the potential impact of Shell and Gulf gas plant operations on surface water quality in the Twin Butte area. The results of these studies provide data on the chemical composition of water in the creeks and lakes in the area. Chemical composition ranges for surface water are given in the Table III-1.

Table III-1 Chemical Composition Ranges for Groundwater and Surface Water Twin Butte - Hill Spring Area

Constituent	Alberta Research Council Analyses				Miscellaneous Groundwater Analyses				Energy Resources Conservation Board				Canadian Drinking Water Standards	
	Groundwater		Surface Water		Complete Analyses		Incomplete Analyses		Groundwater*		Surface Water*		Objective	Maximum Acceptable
	Low	High	Low	High	Low	High	Low	High	Low	High	Low	High		
Calcium (ppm)	0.3	183	14.4	395	2	294.3	7	320	31	93	32	70	-	-
Magnesium (ppm)	<0.1	71	10	158	2	253	0	490	15	63	20	25.5	-	-
Sodium (ppm)	2.0	490	2.1	292	2	821	3	260	9	343	4	6.6	-	-
Potassium (ppm)	0.48	53.0	0.43	53.0	trace	220	2	5	0.7	4.3	0.95	9.1	-	-
Sulfate (ppm)	22.2	1505	<0.10	1456	0.6	2683	0.6	3500	NA		NA		≤150	500
Chloride (ppm)	0.4	46.0	0.20	29.3	0.24	102	0	243	NA		NA		≤250	250
Nitrate (ppm as N)	<0.003	22.5	<0.003	0.124	0.2	134.76	0	156	NA		NA		≤0.001	10
Silica (ppm)	0.32	72.99	0.56	25.0	0.6	31.8	NA	NA	NA		NA		-	-
Fluoride (ppm)	0.11	0.50	<0.03	0.40	0.06	2.11	0.03	0.52	NA		NA		1.2	1.5
Iron (ppm)	<0.01	0.26	0.02	0.22	<0.02	11.79	0	20	ND	1.23	ND	3.6	≤0.05	0.3
Manganese (ppm)	0.006	0.565	0.005	0.404	0.003	0.179	NA	NA	0.005	0.71	ND	0.45	≤0.01	0.05
Total Organic Carbon (ppm)	2.6	6.8	0.4	5.5	NA	NA	NA	NA	NA		NA		-	-
Total Inorganic Carbon (ppm)	26	132	1.5	86.0	NA	NA	NA	NA	NA		NA		-	-
Bicarbonate (ppm)	145	673	7.3	689	65.5	1056	89	895	NA		NA		-	-
Aluminum (ppb)	<1	10	10	40	NA	NA	NA	NA	ND	80	ND	930	-	-
Nickel (ppb)	<1	2	1	2	NA	NA	NA	NA	ND	20	ND	15	-	-
Cadmium (ppb)	<1	1		<1	NA	NA	NA	NA	ND	1.8		ND	≤1	5
Copper (ppb)	<1	17	<1	1	NA	NA	NA	NA	2	480**	ND	30	≤1000	1000
Zinc (ppb)	<1	110	<1	4	NA	NA	NA	NA	10	1430	ND	70	≤5000	5000
Lead (ppb)	<2	5		<2	NA	NA	NA	NA		ND		ND	≤1	50
Chromium (ppb)	<1	1	<1	37	NA	NA	NA	NA	ND	5	ND	3	≤0.2	50
Arsenic (ppb)	<0.2	2.8	0.5	5	NA	NA	NA	NA	ND	3	ND	6	≤5	50
Selenium (ppb)	0.4	1	0.3	1.1	NA	NA	NA	NA	ND	3		ND	≤5	50
Mercury (ppb)	<0.1	0.23	<0.1	0.1	NA	NA	NA	NA		ND		ND	≤0.2	1

NA - not analyzed ND - not detected

* Only natural water samples included in this table. Data on quality of treated (softened) water is given in Appendix H-4, Table 1.

** Sample collected from well at location SE 17-4-29-W4 on April 26-28, 1983 indicated presence of Cu = 2970 ppb. Repeated analyses of the same sample gave results of 2900 ppb (AA) and 3010 ppb (DC Plasma). Results of additional series of analysis for copper in this well are 83-11-14 = 2.938 ppm; 83-11-18 = 0.248 ppm; 83-12-13 = 3.886 ppm and 83-12-29 = 2.962.

Source: TASK FORCE, 1984

Water in the creeks is characterized by a slightly alkaline character (pH ranging from 7.95 to 8.4) and low total dissolved solids (TDS - below 500 mg/L). It represents the calcium-magnesium-bicarbonate hydrochemical type. The only observed exception was an unnamed creek (LSD 16, Sec. 28, Rge. 28, Tp 4, W4M) discharging into the northwest corner of the Waterton Reservoir, where TDS is about 1000 mg/L and the dominant ions are magnesium, sodium, calcium, sulphate and bicarbonate.

Water in the lakes has slightly alkaline to alkaline character (pH ranging from 7.25 to 10.5.) and highly variable total dissolved solids ranging from approximately 130 mg/L (Fish Lake) to approximatley 1600 mg/L (Marna Lake). The dominant hydrochemical type of lake water is calcium-magnesium-bicarbonate/carbonate. Other hydrochemical types of water are also present in the Twin Butte area. These are:

- magnesium-calcium-bicarbonate/carbonate (Marr Lake)
- magnesium-sodium-sulphate-bicarbonate/carbonate (Marna Lake)
- sodium-magnesium-calcium-sulphate (unnamed lake located at LSD 6, Sec. 21, Rge. 28, Twp. 4, W4M).

Surface water in streams exhibits high seasonal variation in chemical composition. The lowest TDS is observed during the spring runoff (snow melt) and probably during the heavy rain periods during summer and fall floods. The highest TDS is observed during the end of winter, when the flow in the creeks is sustained by the groundwater discharge into the creek beds. It is expected that the concentration of

dissolved solids in lakes would also vary seasonally; however, the range of fluctuations is expected to be lower than in the creeks.

Geology

Geological conditions in the Twin Butte area are discussed in the following section.

Bedrock:

The area is underlain by rocks of the Cretaceous System. Locally, the stratigraphic succession ranges from the Lower Cretaceous Blairmore Group - through the Upper Cretaceous Alberta Group and Belly River Formation - to the Bearpaw Formation (G.S.C. 1951).

Stratigraphically, the succession from the Shell plant to the Gulf plant comprises the Blackstone, Bighorn and Wapiabi Formations (Alberta Group) and the Belly River and Bearpaw Formations. The area lies within the disturbed belt associated with Rocky Mountain orogenic events. Consequently, this succession between the Gulf and Shell plants is partially repeated several times by numerous N.W. - S.E. striking thrust faults. Thus, the Shell plant is underlain by rocks of the Wapiabi Formation while the Gulf plant is underlain by strata of the Belly River Formation.

The Blairmore Group subcrops over a relatively large area to the north of the Shell plant. It is about 580 m thick and includes the Crowsnest Formation.

It consists of: basal quartzose sandstone, limestone, conglomeratic sandstones and shales as well as arkosic sandstones. The Crowsnest Formation consists of volcanic tuff and fine agglomerate which are interbedded with shales. Generally, the Group sediments dip relatively gently to the south, but much folding and faulting is evident.

The Blackstone Formation overlies the Blairmore Group and is 107 m thick. It consists mainly of shales and silty and sandy shales. This sequence is followed by the Bighorn Formation which is 24 m thick. It consists mainly of shales and sandy shales. The succession continues with the Wapiabi Formation, consisting of fissile silty and sandy shales. Thin sandstones are also present. This Formation is known to be 230 m thick further to the east of the general area. The Wapiabi Formation subcrops over a relatively large area under and to the southeast of the Shell plant. In the vicinity of the Shell plant, the Wapiabi Formation dips at between 2^{o} - 10^{o} south or southwestward.

The Belly River Formation is about 685 m thick. The lower part consists of transition beds and massive bedded sandstones. The upper part consists of: thick bedded sandstones and interbedded shales; shales and thin sandstone, and coal seams. At the Gulf plant, this sequence is heavily folded and faulted. Both geologic structure and bedding strike N.W. - S.E.. Dips are a comparatively steep 30 - 70^{o}. The regional dip is to the southwest at approximately 30^{o}.

The Bearpaw Formation is approximately 210 m thick. It consists mainly of fissile and silty shales. Some sandy and concretionary zones are present.

Surficial (Quaternary)

A wide variety of surficial deposits are represented in the general area. These comprise pre-glacial (sands and gravels), glacial (clay, silt, sand and gravel tills), glacio-fluvial (outwash and ice-contact silt, sand and gravel), glacio-lacustrine (clays, silts and sands), and recent fluviatile and lacustrine deposits.

The deposits at or near the plant sites are predominantly till. The till is variable in thickness; in fact, bedrock is exposed in the vicinity of both plant sites. The till is mainly hummocky moraine and ground moraine. Hummocky moraine is present at the Gulf site and the till includes minor gravel, sand and silt lenses. At the Shell site, the hummocky moraine is represented by silt and sand. Ground moraine is also present at the Shell site and consists of silt, sand and gravel.

According to Geiger (1965) a number of minor pre-glacial valleys are present on the bedrock surface in the vicinity of the plant sites. Surficial deposits may be as much as 60 m thick in these valleys (Geiger 1965). Permeable sand and gravel may overlie bedrock at these locations. Such material may form local strip-aquifers. They may be continuous over relatively large distances.

Alternatively, they may impinge on and be terminated by present day valleys.

Conversely, in certain parts of the area, surficial deposits are only a thin veneer of till (Stalker, 1956). Bedrock is occasionally exposed, particularly in river valleys.

Hydrogeology

Hydrogeological conditions in bedrock and surficial (Quaternary) deposits are presented in the following section.

Bedrock:

The hydrogeological conditions in the bedrock (Lower and Upper Cretaceous formations) underlying the Quaternary deposits are practically unknown. There are very few properly documented water wells completed in the bedrock. The groundwater may be present in the sandstone, limestone, conglomeratic sandstone and weathered or structurally disturbed shale/siltstone layers. These formations are usually characterized by low to medium hydraulic conductivities. Therefore, the available groundwater resources are limited. Groundwater quality near the bedrock surface is expected to be satisfactory to good. With depth, the total dissolved solids content will increase, making the water less suitable for human consumption.

The bedrock aquifers are separated by thick sequences of very low hydraulic conductivity shales.

Surficial (Quaternary)

The groundwater occurrence in the Quaternary deposits and expected yields are highly variable. The main aquifers in the Twin Butte area are present in:

1) preglacial buried channels filled with sands and gravels (eg. channel near Waterton Dam - Tp 4, Rges 27 and 24, W4M, channel near Gulf Plant - Tp 4, Rge 29, W4M, etc.)

2) alluvial deposits along the major rivers and creeks (eg. Waterton River, Drywood Creek).

Locally, domestic water supplies may be obtained in this area from silty sand and gravel layers or lenses occurring within the till deposits (ground and hummocky moraine).

The groundwater surface in the surficial deposits stabilizes usually within 5 m below ground surface. Locally, especially in the valleys, artesian conditions may be encountered.

The groundwater quality depends on many factors; climatic conditions, lithology of deposits in which groundwater is present, and circulation conditions. Since most of the wells tested in the area are relatively shallow (less than 100 m deep) it was assumed that the samples represent groundwater occurring within a zone of active water exchange. This assumption was later confirmed by the environmental isotope study. A lack of geological logs for most of the wells makes it

impossible to differentiate between samples collected from Quaternary and Cretaceous deposits. Most of the wells are completed in the Quaternary deposits, with only few reaching the bedrock.

The water yielding characteristic of Quaternary sediments depends on the thickness of the deposit, hydraulic conductivity, lateral extent, terrain topography and recharge conditions. The hydraulic properties of these deposits vary from medium hydraulic conductivity silty sands and gravels to low hydraulic conductivity till and clay deposits. The presence of different types of deposits affects the groundwater recharge and circulation conditions. These variable conditions contribute to the presence of different hydrochemical types of groundwater in the study area. Chemical composition ranges for groundwater are given in the Table III-1.

The majority of groundwater samples represent the calcium-magnesium-bicarbonate type. Less common are the calcium-magnesium-sulphate, sodium-sulphate and sodium-bicarbonate-sulphate types. The total dissolved solids range from approximately 300 to 5,000 mg/L. Groundwater has a slightly alkaline to alkaline character with pH varying between 7.0 and 9.6.

Groundwater with high TDS usually has high SO_4 content, which may exceed 3,500 mg/L (maximum acceptable for drinking water is 500 mg/L). Chloride concentrations in groundwaters present in the study area are very low.

Nitrate concentrations in many shallow wells and springs are very high, reaching 156 mg/L (as N). Domestic sewage and seepage from barnyards are common sources of nitrates in the groundwater in the rural areas. Other sources of nitrates may be fertilizers and industrial plant effluents. According to information obtained from the local residents, use of fertilizers in the study area is very limited. The concentration of nitrates in the Shell Plant effluent is usually low and does not exceed 10 mg/L. Hendry et al. (1984) determined that the high nitrates found below groundwater surface in the weathered till are the result of the oxidation of ammonium present within the tills. Nitrate concentrations in groundwater samples collected in southern Alberta may exceed 300 mg/L. Other potential sources of nitrates in groundwater may be improper sewage disposal practices and/or ranching activities.

Iron and manganese are very common constituents of groundwater in the study area with maximum concentrations of 20 mg/L and 1 mg/L respectively. These values exceed maximum acceptable concentrations for drinking water, which are 0.3 mg/L for iron and 0.05 mg/L for manganese.

Other trace elements (eg. mercury, cadmium, chromium, lead, arsenic) were found in groundwater at concentrations that in general did not exceed Canadian Drinking Water Standards. Higher concentrations of toxic metals such as lead, chromium and cadmium were detected in groundwater samples on isolated occasions in different wells. Some of the wells were sampled several times with only one analysis indicating anomalous high

concentrations of a particular element. These anomalies may be attributed either to erroneous analyses or improper sampling techniques which led to sample contamination.

GAS PLANT SITES

Available information on the Geology, Surface Water and Hydrogeology at the Shell Waterton Gas Plant and the Gulf Pincher Creek Gas Plant are summarized below:

Shell Waterton Gas Plant

A detailed evaluation of geological, surface water and hydrogeological conditions at this plant is given in Appendix H-1.

The bedrock consists of silty and sandy shales with thin sandstone beds of the Wapiabi Formation (Upper Cretaceous). These sediments are covered with a thin (less than 10 m) layer of the Quaternary deposits consisting of glacial till, sandy silt and sand layers.

Several process waste water and surface runoff ponds were constructed within the plant site boundaries. Chemical composition of water in the basins varies within a wide range from fresh (total dissolved solids below 1,000 mg/L) to brackish (TDS below 10,000 mg/L). The pH ranges from 2.06 (Basin No. 1) to 9.91 (Basin No. 6). The dominant ions are sulphate, chloride, bicarbonate, sodium, calcium and magnesium. All basins tested by Shell indicate very low metal concentrations.

A discharge of slightly brackish Shell plant effluent with total dissolved solids ranging from 1334 to 3594 mg/L

increases the amount of dissolved matter in the North Drywood Creek to a maximum measured level of 1357 mg/L (83.02.09) below the effluent discharge point. Further downstream at the Highway #6 crossing, the TDS ranged from 210 to 818 mg/L. The background level of total dissolved solids measured in the creek was 229 to 349 mg/L. An increase in calcium, sodium, sulphate and chloride concentrations is observed immediately below the Shell Plant effluent discharge point. The concentration of these ions decreases gradually due to dilution downstream. The plant also introduces nutrients to the North Drywood Creek. Above the discharge point, concentrations of ammonia and phosphate are below the detection limits (for both compounds 0.1 mg/L) while below the discharge point, their concentrations vary as follows:

ammonia - below detection limit to 0.3 mg/L
phosphate - 0.2 to 2.3 mg/L.

The presence of nutrients encourages algal growth in the stream water.

The increase in trace element concentrations in the North Drywood Creek is difficult to define since in many instances, concentrations of these elements in the effluent are very low. According to the available chemical analyses, an increase in the following trace element concentrations was observed below the Shell plant discharge point. These were: arsenic, boron, selenium, zinc, lead, and nickel, with only selenium and arsenic exceeding the maximum acceptable concentrations for drinking water. Further downstream, at Highway #6 crossing, concentrations of both selenium and arsenic were always below the maximum acceptable for drinking water.

High concentrations of arsenic in the Shell plant effluent were traced to the gas well Waterton #42. To avoid surface water contamination in the future, formation water from the Sheet IV wells is injected into a deep disposal well.

Very small quantities of cyanide (0.05 to 0.07 mg/L) were observed in the plant effluent in the spring of 1983. The cyanide concentration rose from less than the detection limit (0.01 mg/L) upstream from the plant to 0.02 mg/L in the stream below the discharge point. This value is an order of magnitude lower than the maximum acceptable concentration for drinking water.

The knowledge of hydrogeological conditions at the Shell Waterton gas plant is limited. Therefore, it is not possible to define the existence and extent of potential groundwater contamination zones within the plant area.

Terrain topography (largely flat areas) and the presence of permeable deposits (gravel, sand and silt) on the ground surface indicate the potential for groundwater contamination as a result of accidental spillage of chemicals or seepage from the retention ponds. Installed piezometers appear to indicate certain groundwater contamination in the plant area which is expressed by variable main ion composition, higher TDS, elevated levels of nitrate/nitrite, high iron, manganese and locally chromium concentrations. These parameters are different from those observed in springs and seeps not affected by the plant operation.

A review of the available geological and hydrogeological information indicates that the groundwater flow from the majority of the Shell plant area is directed toward the North Drywood Creek Valley. Localized areas may also be drained towards the north and east of the plant. The quality of water in a spring located south of the plant in the North Drywood Creek Valley (Spring No. 1) has been affected by seepage from the sulphur block surface run-off pond. It exhibits very high sulphate concentrations (over 1,000 mg/L) and higher concentrations of main ions in comparison with other springs and seeps monitored.

Groundwater monitoring systems, established by Shell in 1983, should be expanded by installation of additional piezometer nests required to define and to delineate the extent of the contaminated groundwater zones.

During the operations of the Shell Waterton plant, industrial wastes have been disposed of within the plant site in different locations. Very limited information regarding volume and contents of these sites is available. Therefore, it is recommended that a detailed survey of solid waste disposal sites be made and that appropriate groundwater observation systems be established to monitor potential leachate movement.

The Task Force study (Chapter 5) confirmed the presence of organic compounds in the gaseous emissions from the Shell Waterton Plant. Previous studies did not include an evaluation as to the extent and concentrations of organic compounds in surface water and groundwater. Since organic compounds in the air are present in very small quantities, their concentrations in the waters are expected to be very

low also. Despite that, a survey of surface water and shallow groundwater should be conducted to determine the presence and concentrations of these compounds.

The Task Force concluded a preliminary groundwater sampling program to determine presence of organic chemicals at the Shell plant. Five piezometers and one spring were sampled and water analyzed.

Groundwater at four locations immediately north and east of the processing facilities and ponds at the Shell plant was contaminated with sulpholane, a process chemical, in concentrations up to 100 ppm. A natural water seep 1 km west of the plant reservoir contained no sulpholane (see Appendix H-1).

Although sulpholane is essentially non-toxic*, its use as a solubilizing agent in the plant process suggests that other, potentially more toxic compounds might enter groundwater in conjunction with it.

The only other organic chemical besides sulpholane that was detected by GC/mass spectrometry in appreciable concentrations (a few parts per million) was a compound of molecular weight 157 and molecular formula $C_7H_{11}NO_3$ which is suspected of being a cyclic oxidation product of di-isopropanolamine, a process chemical used in conjunction with sulpholane itself.

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*Sulpholane has an LD_{50} value (oral, rat) of 1500 mg/kg body weight (aspirin has an LD_{50} of 1000 mg/kg) whereas a recent article (Langley, 1984) suggests that all compounds that are non-fatal when fed at 5 mg/kg should be classified as non-toxic, thereby avoiding the need for the inhumane determination of an LD_{50} value.

Only traces of other compounds were detected in groundwater samples taken in June 1984, but a more extensive set of piezometer nests should be installed to permit monitoring of groundwater at the Shell plant in future, paying particular attention to sulpholane and associated compounds, and in order to delineate the extent of contaminated groundwater zones.

Gulf Pincher Creek Gas Plant

A detailed evaluation of geological surface water and hydrogeological conditions at this plant is given in the Appendix H-2.

The bedrock in the Gulf plant area consists of: sandstones with interbedded shale, massive marine shales, thin bedded sandstone of the Belly River Formation (Upper Cretaceous). A broad channel eroded in the bedrock, extends below the plant site. It is filled with a preglacial gravel deposit (Quaternary) 1 to 5 metres thick. These sediments are covered by a thick layer (30 to 42 m) of silty clay till.

The study conducted by Monenco Consultants Ltd. at Gulf's Pincher Creek Gas Plant (1983) indicates the presence of brackish water in some ponds. Dominant ions are calcium, magnesium, sodium and sulphate with the last reaching concentrations in the order of 4,000 mg/L in the sulphur block runoff pond (Pond 8). The ammonia-nitrogen concentrations in Pond 9 substantially exceed the background levels.

Samples taken by Monenco from the ponds for trace element analyses were not filtered. Therefore, the results may not represent the concentrations of dissolved elements.

In the sulphur block runoff pond, where water is highly acidic (pH = 2.2), the concentrations of all tested trace elements, with the exception of barium, substantially exceeded the background levels. Similar results were obtained from the lake located southwest from the solid waste disposal pit. Other reservoirs (Ponds 6, 7, Pond 6 weir and Pond 9) contain water with iron, manganese and chromium concentrations higher than observed in the control samples.

The highest cyanide concentrations were observed in Ponds 6 and 9 and the surface drainage channel south of the landfill area (maximum - 0.001 mg/L). Even such a low concentration appears to be slightly higher than those observed in surface water samples collected in the adjacent areas.

The hydrocarbon concentrations measured in on-site ponds are similar to those observed in the off-site water samples.

During the course of the Monenco study (1983), no water from the retention ponds was discharged to the surface drainage system. Therefore, no data on water quality in the Drywood Creek below the discharge point is available.

The water stored in ponds on the Gulf plant site contain high concentrations of different trace metals. Therefore, it should not be released to the surface drainage system without an appropriate treatment.

According to the Gulf records, an uncontrolled release of water from Ponds 7 and 8 occurred in May 1981. As a result of unusually high precipitation (approximately 100 mm), the plant surface runoff holding capacity was reduced to zero.

It forced water diversion from Pond 7 to Pond 8 as well as release of water to the Drywood Creek. Accumulation of water in Pond 8 caused a dyke failure on May 22, 1981, which resulted in uncontrolled release of approximately 35,000m^3 of water into the natural drainage system. It was estimated by the plant operator that 70 to 80% of this water originated from Pond 7. The result of water sample surveys collected from Pond 7 on May 19, 1981 are as follows: pH - 6.6, Chemical Oxygen Demand (COD) - 75 mg/L, total sulphides - less than 0.01 mg/L, oils and greases - less than 1 mg/L, ammonia - 2.4 mg/L, threshold odour number - 1, and suspected solids - 4 mg/L. Similar results were obtained on May 21 and 25, 1981.

The Gulf Pincher Creek Gas Plant is situated in an area where a thick layer (30 to 42 m) of silty clay till of low hydraulic conductivity overlies the older sediments. In this area, movement of contaminants would be relatively slow and, in most cases, restricted to the upper water bearing zone. Higher hydraulic conductivity lenses (more silty or gravelly layers) were found throughout the till. It is believed that these layers are discontinuous and are not hydraulically connected.

The areas of groundwater contamination due to plant activities and seepage from the ponds within the Gulf property are delineated in the Monenco Reports #5 and #6. The available data indicate that the zones of contaminated water are localized within the plant boundaries.

Monenco investigations (April 1984) defined the sub-areas within the plant site where significant contamination of groundwater occurred. These are:

Sub-Area 1

sulphur plant and sulphur block: main contaminant is sulphate.

Sub-Areas 9 and 10

natural gas liquids and loadout facility: main contaminants are benzenes and various polycyclic aromatic hydrocarbons, and chloride.

Sub-Area 3

treater building: main contaminants are total organic carbon, organic nitrogen and ammonia.

Sub-Areas 5 and 6

inlet building and hydrocarbon building: contamination with hydrocarbons is suspected based on soil samples evaluation.

Sub-Area 7

classifier: main contaminants are hydrocarbons and nitrogen compounds.

The Monenco report points out that the description of groundwater quality in the sub-areas is based on a limited number of groundwater samples and additional sampling may be required to delineate the contaminant extent.

In general, trace element concentrations reported by Monenco indicate relatively high concentrations of cadmium (Cd), chromium (Cr), mercury (Hg) and lead (Pb) in the plant site. These concentrations are much higher than control (background) data obtained by ARC (Appendix H-3) and ERCB (Appendix H-4) even though the latter samples were not filtered prior to acidification. Organic compounds of concern were also detected in some areas. These include benzene and various polycyclic aromatic hydrocarbons.

All existing data on organic chemicals in groundwater on or near the Gulf plant site were summarized in a memorandum from Monenco Consultants Ltd. to Gulf Resources Ltd. (see Appendix H-2).

Groundwater at the Gulf plant was severely contaminated directly beneath a waste pit used for unflared residues for many years. Fortunately, this contamination is centrally located on the site. Other groundwater samples from the plant sites were considerably less contaminated, and samples taken from the site periphery or off-site had little or no contamination with organic material.

The only area beyond the plant site boundary where higher sulphate and total dissolved solids concentrations were observed, which may originate from the plant operation, lies southeast of Pond 8. The hydrochemical anomaly was documented to extend over 100 m beyond the plant limits within the upper aquifer. In the same area, a piezometer (29-1) installed within the preglacial gravel deposits underlying the till deposits (lower aquifer) indicates the presence of groundwater with raised total dissolved solids

and sulphate concentrations. The origin of these anomalies should be investigated further by Gulf to determine the source of the anomalous sulphate concentrations. If the anomalies in both aquifers are related to the plant operations, it would indicate that in the general area of Pond 8, a hydrogeological window exists, which allows groundwater movement from the upper aquifer through the till into the lower aquifer.

During the past exploration programs, a number of piezometers were installed in the plant area. The existing groundwater observation network will be supplemented by Gulf with additional piezometers in the future. Selected piezometers will be utilized as permanent groundwater monitoring points.

TASK FORCE EXPLORATION PROGRAMS

This section of the report outlines the field and laboratory exploration program undertaken by the Task Force.

The Twin Butte Soils and Water Evaluation Task Force contracted Alberta Research Council, Natural Resources Division to collect surface water, groundwater, soil and air moisture samples in the study area, distribute samples to laboratories for chemical analyses, conduct artificial weathering tests and summarize findings in a technical report (Appendix H-3). The study results are summarized below.

Field Sampling Program

The water and soil sampling program was conducted between September 12 and September 23, 1983. Sample collection,

preparation, preservation and storage was conducted according to the guidelines developed jointly by the ARC and Task Force representative. It was essential for this project to obtain the highest quality samples, therefore, ultra clean methods of water sampling were applied.

There were few changes from the originally planned well sampling locations. In some cases the well sampling location was altered to match the vegetable sampling point (see Chapter Four of this report). In one instance, the well owner refused sampling of the well and in another case no one was home during the sampling period.

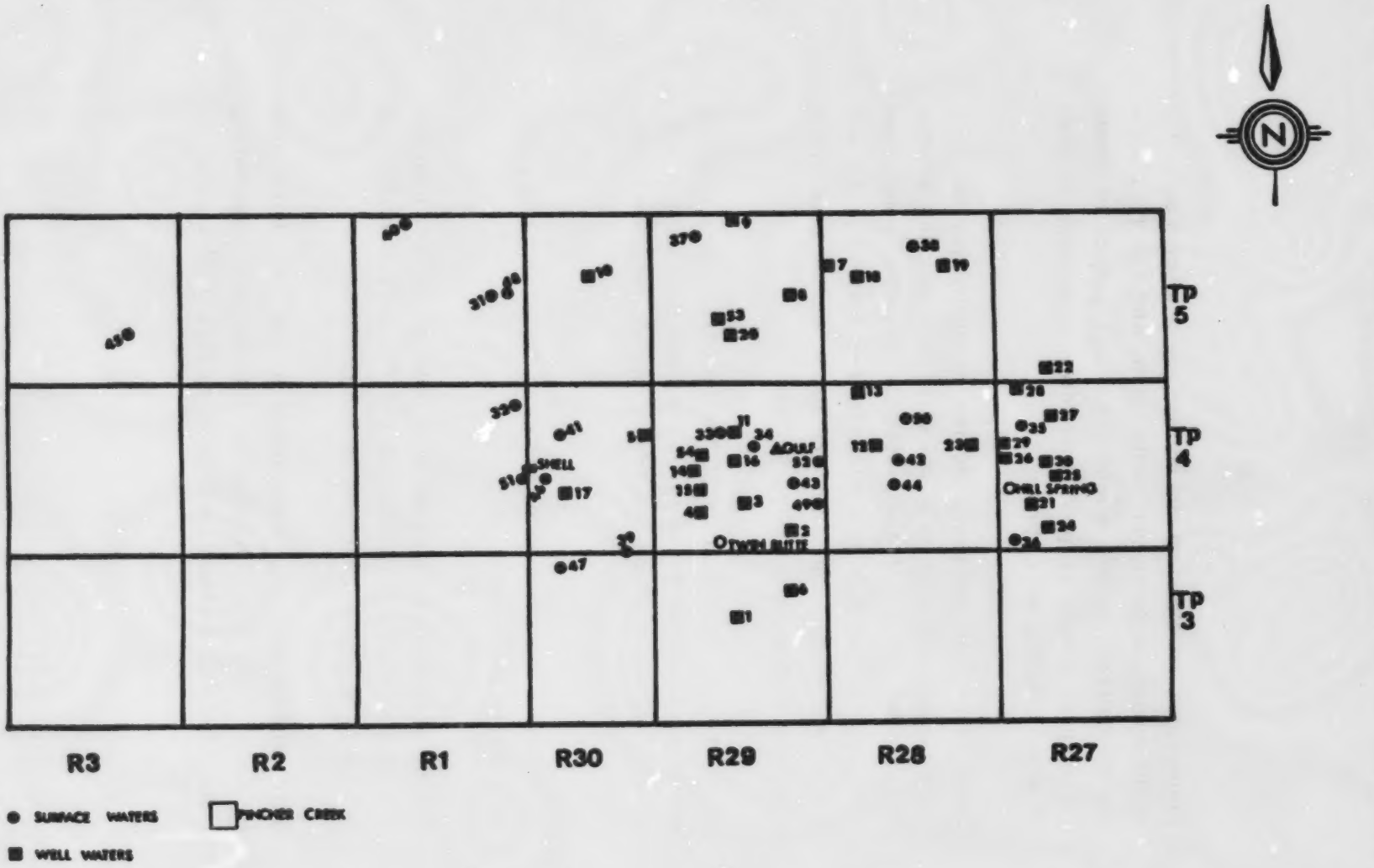
In addition to the originally planned program, four sampling points were selected following the recommendations of Mr. A. Bonertz and Mr. L. Hochstein (September 15, 1983, Task Force Meeting).

The location of surface water and groundwater sampling points is shown in Figure III-3.

Atmospheric moisture samples were collected at five locations downwind from the Shell Waterton Gas Plant. The locations of the sampling points are shown in Figure III-4.

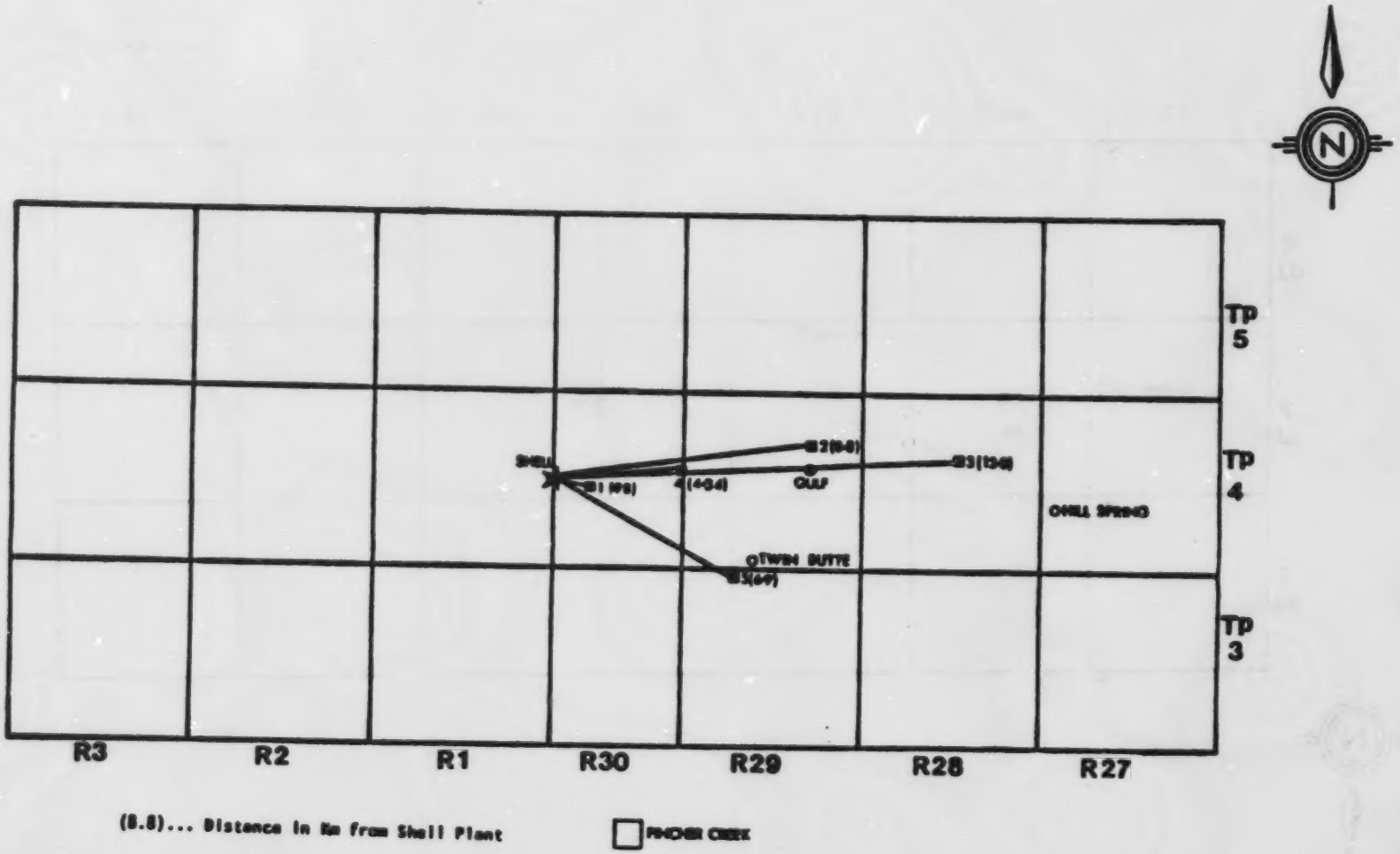
Three shallow boreholes were drilled in the Twin Butte area to collect soil and till samples for artificial weathering tests. Borehole locations are shown in Figure III-5.

FIGURE III-3 DISTRIBUTION OF SAMPLE POINTS FOR GROUNDWATER AND SURFACE WATER.



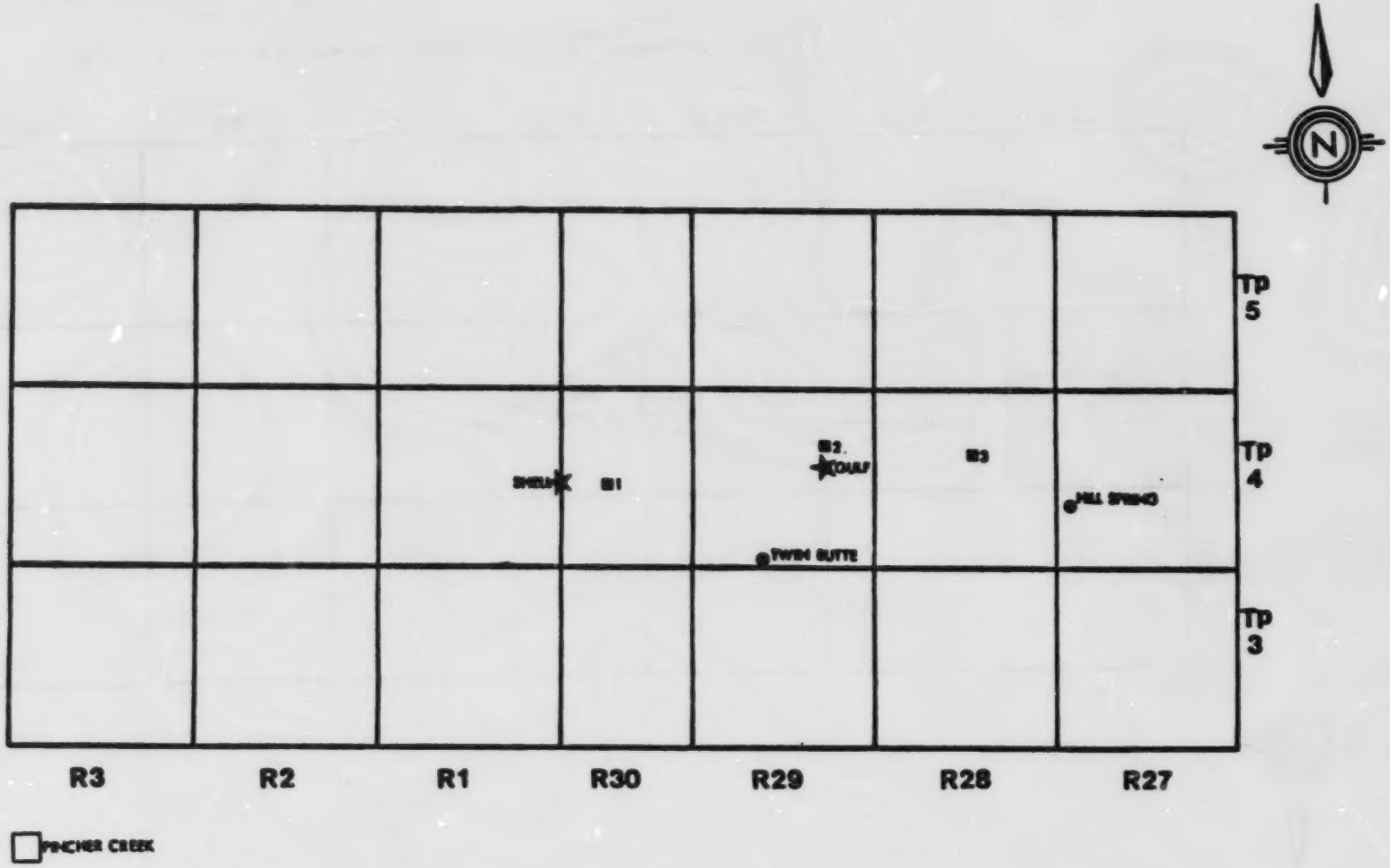
SOURCE: Alberta Research Council Report, 1984, Appendix H-III.

FIGURE III-4 DISTRIBUTION OF ATMOSPHERIC MOISTURE SAMPLING SITES.



SOURCE: Alberta Research Council Report, 1984, Appendix H-III.

FIGURE III-5 DISTRIBUTION OF SOIL AND TILL SAMPLING SITES.



SOURCE: Alberta Research Council Reoprt, 1984, Appendix H-III.

Laboratory Program

Surface water and groundwater samples were analyzed for major and minor constituents to establish the local hydrochemical background. The analyses were performed by Chemex Laboratories in Calgary. Selected samples were tested by Alberta Research Council, Chemistry Laboratory for interlaboratory comparison. For most of the constituents, the difference is less than 10 percent. That is within acceptable limits.

Water samples were also tested for trace metal concentrations by Chemical and Geological Laboratories in Edmonton using inductively coupled plasma analyses (I.C.P.). This method was applied as a scan to define the presence of trace elements in tested waters. Another purpose for using the I.C.P. method was to assess its suitability for similar hydrochemical studies. The I.C.P. results indicated high cadmium concentrations in a few instances. Based on these results, six samples with high cadmium concentrations and six samples with low cadmium concentrations were selected for atomic absorption analysis, to confirm the I.C.P. analysis results. The atomic absorption analyses were performed by Chemex Laboratories in Calgary.

The atomic absorption spectrometry (A.A.) did not confirm the presence of cadmium in either the high or the low cadmium concentration group as defined by the I.C.P. method. Comparison of cadmium and other element analysis results

indicates that the detection limits of the A.A. method are lower by a factor of ten or more than those of the I.C.P. method. However, interferences observed with the latter method cause severe limitations of application of this method in hydrochemical studies requiring high quality results.

Analyses of atmospheric moisture, conducted by Chemex Laboratories included determination of the following anions: Cl, NO_3 and SO_4. The purpose of these analyses was to evaluate the suitability of this method for hydrochemical studies and to determine whether levels of SO_4 show any relation to gas plant emissions.

Tests of soil and till for chemical weathering potential were conducted by the Alberta Research Council. The release of major, minor and trace chemical constituents by exposure to SO_2 was evaluated using a technique developed by E.I. Wallick and M.H.R. Huemmert (1982) for modelling the weathering of overburden materials from surface coal mines.

Analyses of the stable isotope composition of hydrogen, oxygen and sulphur on water samples were performed at the Physics Department of the University of Calgary by Dr. A. Shakur of the Alberta Research Council.

The tritium content in water samples was determined at the Geochronology Laboratory, Alberta Environmental Centre in Vegreville under supervision of Dr. L. D. Arnold.

Chemical and Isotope Analysis

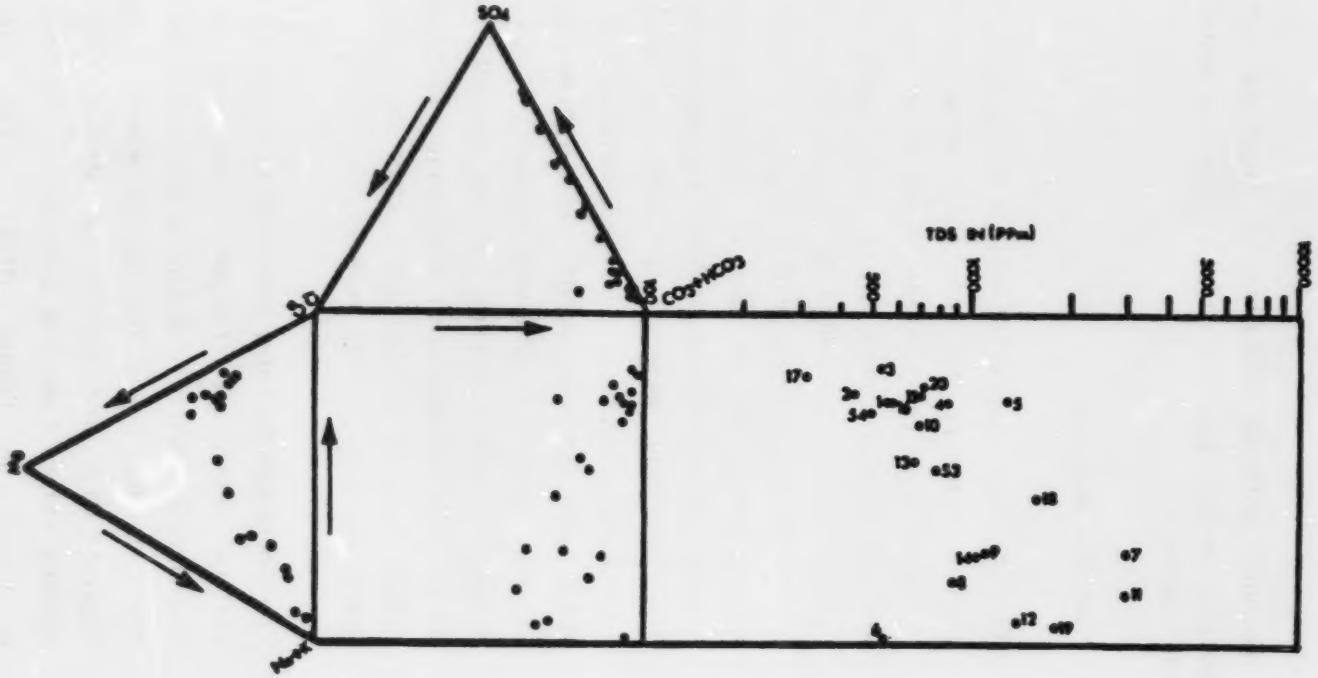
This section outlines results of analyses of trace constituents, isotope geochemistry, atmospheric moisture and chemical weathering.

1. Chemical Analysis

The chemical composition ranges for groundwater and surface water in the Twin Butte area are given in Table III-3. Total dissolved solids of groundwater are within the range 300 - 3,000 mg/L while for surface water, the range is 30 - 2,000 mg/L. The major ion composition varies within a wide range. Approximately 80% of samples tested represent the bicarbonate-calcium-magnesium hydrochemical type. The remaining waters represent the bicarbonate-sulphate-sodium, bicarbonate-sulphate-calcium-sodium, sulphate-bicarbonate-sodium and sulphate-magnesium-calcium types. Chloride concentrations in all sampled waters are very low and do not exceed 46 mg/L. The concentration of sulphates in groundwater ranges from 12 to 1500 mg/L while in surface water this range is from 1 to 1445 mg/L.

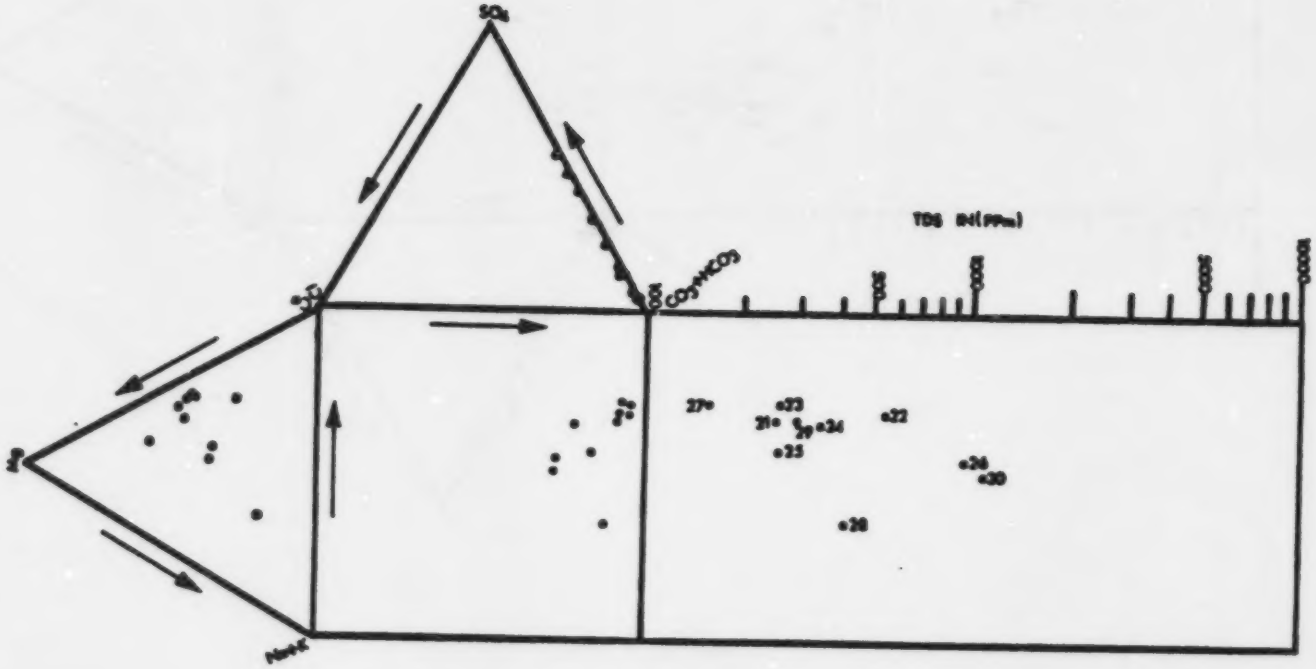
The pH of groundwater ranged from 7.2 to 8.2 and for surface water it ranged from 7.3 to 10.0. The distribution of chemical groundwater types from the Twin Butte and Hill Spring areas is shown on Figures III-6 and III-7. A similar diagram for surface waters from the Twin Butte-Hill Spring area is shown on Figure III-8. The overlapping composition and concentration ranges may indicate

FIGURE III-6 GROUNDWATER CHEMICAL COMPOSITION - TWIN BUTTE AREA.



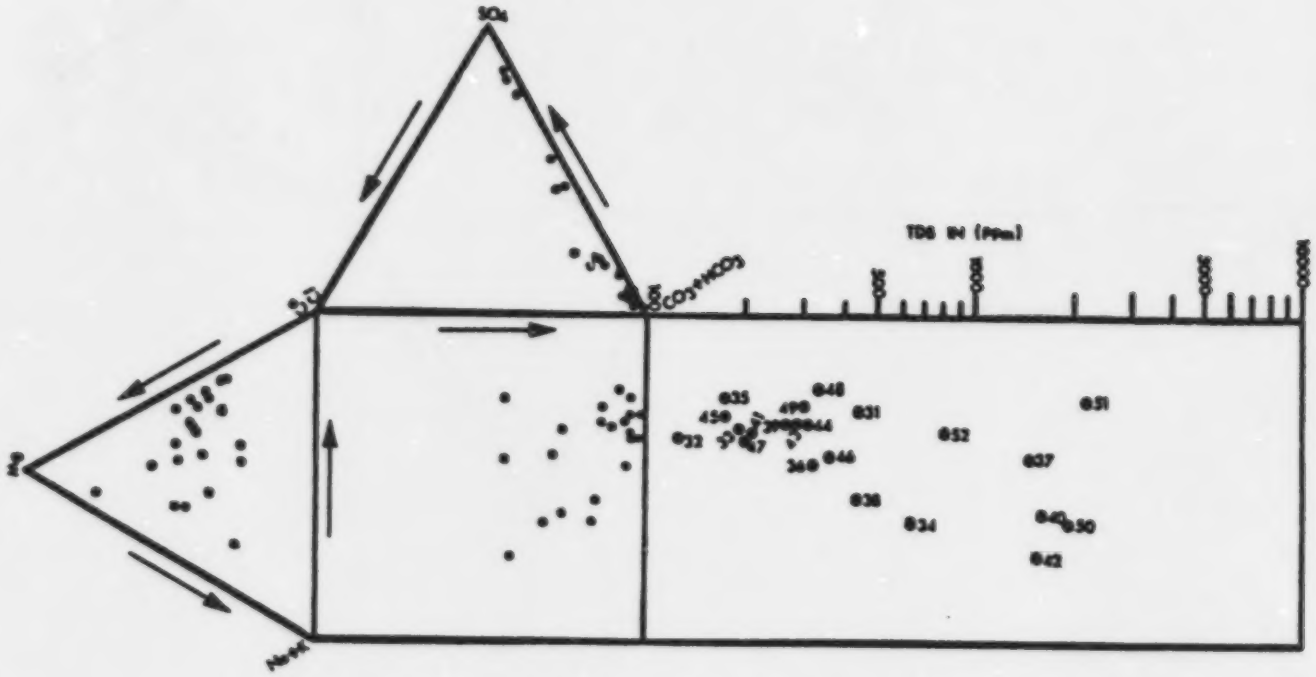
SOURCE: Alberta Research Council Report, 1984, Appendix H-III.

FIGURE III-7 GROUNDWATER CHEMICAL COMPOSITION - HILL SPRING AREA.



SOURCE: Alberta Research Council Report, 1984, Appendix H-III.

FIGURE III-8 SURFACE WATER CHEMICAL COMPOSITION.



SOURCE: Alberta Research Council Report, 1984, Appendix H-III.

that there is a hydraulic connection between surface water and shallow groundwater occurring in the study area. Chemical characteristics of the water are quite typical for a southern Alberta region covered by glacial till containing carbonates and organic-rich shales.

With the exception of manganese, other minor and trace constituents were not found in the groundwater and surface water in concentrations that exceeded maximum acceptable levels for drinking water.

A review of the hydrochemical data indicates that the chemical composition of the surface water and groundwater was not affected in any systematic way by either gas plant.

2. Isotope Geochemistry

Environmental isotopes of hydrogen, oxygen and sulphur were studied to determine water origin and movement as well as to trace sulphur originating from gas plants through the surface water and groundwater systems. The results of the analyses indicate that the surface water system is hydraulically connected with the shallow groundwater system. Tritium content suggests that the majority of groundwater samples tested are possibly less than 15 years old. The wide range of tritium values in surface waters may result from a variable contribution of the groundwater.

Elemental sulphur originating from the gas plants accumulates on the ground surface and in surface water very close to the plant. There is no evidence that sulphur dust and/or SO_2 emissions visibly affected the surface water or groundwater quality.

3. Atmospheric Moisture

Samples of atmospheric moisture were collected downwind from the Shell Waterton incinerator stack. The sulphate concentrations measured decrease with the distance from the plant. Closest to the plant SO_4 concentrations were 0.5 mg/L while at the farthest point, 0.2 mg/L. This range of values is representative for snow samples collected in Alberta and southern British Columbia (P. W. Summer and B. Hitchon, 1973).

4. Chemical Weathering Potential

The purpose of this laboratory experiment conducted by Dr. E. I. Wallick (Alberta Research Council) was to define the potential for the release of toxic heavy metals from local till material in the SO_2 enriched atmosphere. If the release of heavy metals from till were found to occur at SO_2 concentrations much higher than those present in the vicinity of the sour gas plants, the position could be taken that given sufficient time, the metals would be leached at much lower concentrations of SO_2 in the air.

The weathering experiments were conducted on six till samples over 16 days in a control and in a variable atmosphere chamber. Only one sample shows a noticeable drop in pH (2.4) under an atmosphere containing 0.34 percent by volume of SO_2. This indicates a lower buffering capacity of this particular sample till. The drop in pH was associated with an increase in trace metals concentrations. The trace metals released were not at a toxic level, even at a pH as low as 2.4.
The results indicate that the release of trace metals may occur at very high concentrations of SO_2. The remaining five samples showed a decrease of pH from approximately 9 to 7. At this pH level, no increase in trace elements concentrations could be observed.

The gaseous emissions from the incinerator stack are dispersed into the atmosphere. The SO_2 concentrations in the weathering chamber are therefore several hundred times higher than the SO_2 concentrations (in the order of 0.02 mg/L) observed in the air in the vicinity of the plant. Making simplifying assumptions, a one-day test at an SO_2 concentration of 34 mg/L may be considered as equivalent to 1700 days (approximately 4.6 years) in the field conditions. For higher SO_2 concentrations (3400 mg/L) a one-day test would be equivalent of 465 years.

The most important observations based upon the analysis of six till samples from the Twin Butte area are that a threshold partial pressure exists below which there is little or no reaction of SO_2 with an

aqueous suspension of soil/till, and that the release of trace metals can occur only if the pH of the soil water system falls to 3.0 approximately. The threshold value of the partial pressure of SO_2 lies between 34 mg/L and 3400 mg/L (0.34 percent) for the materials studied. Increasing amounts of organic carbon, calcium, sulfate, silica, copper, lead, cadmium, cobalt, nickel, manganese, vanadium, chromium, strontium, aluminium, and zinc were released upon exposure of a shallow till sample to 0.34 percent SO_2 by volume.

WATER QUALITY IN THE TWIN BUTTE AREA

Water quality was sampled throughout the Twin Butte Area. Tests were made of tap water, groundwater and surface water.

Tap Water Sampling Program

The tap water sampling program conducted in 1983 by the Energy Resources Conservation Board included over 30 water supply sources. The methodology of sampling, analytical techniques and the results of analyses are given in the Appendix H-4 and summarized below.

Main cations: calcium, magnesium, sodium and potasium are present in quantities characteristic of the southwestern part of Alberta.

Minor elements: iron and manganese are abundant in both surface water and groundwater in this region and their presence in high concentrations is not related to the sour gas plant operation.

The concentrations of trace elements of cadmium, copper, lead, chromium, zinc, arsenic, selenium and mercury were determined in all water samples. The results indicate that most trace elements present in drinking water are well below their recommended maximum concentration according to the Guidelines for Canadian Drinking Water Quality (1978). The only exception encountered was the copper concentration in the shallow well located SE 17-4-29 W4, which varied from 220 to 3,886 ppb. The maximum acceptable copper concentration in drinking water is 1,000 ppb (1 ppm or mg/L). Fluctuations in copper concentrations in this well are difficult to explain based on the available data. A wide range of copper concentrations in the samples tested may be related to the sampling method. It is our understanding that the E.R.C.B. is conducting further studies to determine the origin of high copper concentrations in this particular well.

Miscellaneous Surface Water and Groundwater Analyses

To supplement the available information on water quality in the Twin Butte area, the results of the studies conducted by Government agencies and a number of scientific reports were evaluated. These are briefly described in the following section. All of the background information is included in the Appendix H-5.

Evaluation and comparison of hydrochemical data collected during a number of different studies is a difficult task.

Sampling points are in many instances different, samples may be collected during different periods of a year and sampling as well as analytical methods may vary considerably.

Most of the available data does not include descriptions of the sampling techniques. If water samples were collected without filtering, substantial variation in chemical composition may occur, even if water is apparently free of suspended solids. The most significant differences will occur in the concentrations of the trace elements (e.g. heavy metals). The quality of chemicals used for sampling preservation, storage and time elapsed between sampling and testing may have also an impact on the analytical results.

It should be noted that the following evaluation is based on hydrochemical data, which in some instances may be considered incomplete and possibly of questionable quality. Despite these reservations, it was decided that all the data available for the Twin Butte area should be included in the Task Force study.

Groundwater samples from four piezometer nests near ponds at the Shell Waterton plant were obtained in June, 1984 by Monenco Ltd.

Samples were shipped in glass bottles to Envirotest Labs, Edmonton where they were extracted with hexane and concentrated by evaporation. Preliminary chromatograms were obtained using a "Carbowax" column and flame ionization detector; individual components were then more positively identified by GC mass spectrometry.

1. Surface Water

The water quality in the creeks flowing through the study area exhibits seasonal variation. The effects of the sour gas plant operations on water quality are only visible in the North Drywood Creek, immediately below the Shell gas plant, where a slight increase in Total Dissolved Solids (TDS), bicarbonate (HCO_3), sulphate (SO_4), chloride (Cl), sodium (Na), potassium (K) and nitrate (NO_3-N) may be observed. Further downstream, due to dispersion, the main ion concentrations are reduced to approximately background levels. Trace element concentrations in this creek are within the background range. The only exception was observed in spring of 1983, after elevated arsenic concentrations were discovered in the effluent from the Shell plant.

2. Groundwater

The groundwater quality is highly variable in the study area. It ranges from bicarbonate-calcium-magnesium water suitable for human consumption with TDS below 500 ppm to sulphate-sodium waters with TDS exceeding 1000 ppm, which is not suitable for human consumption according to Canadian Drinking Water Quality Guidelines.

Nitrate concentrations in groundwater observed in many shallow wells and springs are extremely high, which makes them unsuitable for human consumption. Iron and manganese concentrations are commonly high,

exceeding the acceptable limits for the drinking water. These elements are abundant throughout the Quaternary deposits present in the Twin Butte area, and therefore their presence in groundwater may be considered a natural phenomenon.

Barium and fluoride concentrations rarely exceed the maximum acceptable for drinking water. Slightly elevated concentrations of these elements in the study area are most probably due to the presence of barium and fluorine containing minerals in the surficial deposits.

Only in one instance, and in different wells, were lead, cadmium, and chromium concentrations detected above the maximum acceptable levels for drinking water. These anomalies cannot be explained based on the existing data.

CHAPTER FOUR

METALS AND SULPHUR ISOTOPES IN SOIL, VEGETATION & SEDIMENT

This chapter contains the background to work commissioned by the Task Force, the rationale for that work and the methods and results of analyzing for metals and sulphur isotopes in soil, vegetation and sediment in the Twin Butte area.

BACKGROUND

The background section of this report reviews previous studies of metal concentrations in the Twin Butte area and explain the need for further information.

Previous Reports on Metal Concentrations

On May 17, 1983 (which also happened to be the date of the Twin Butte Task Force's second meeting), the Edmonton Journal carried the main headline "Cancer Link to Gas Plants" and a front-page summary of the report by Snider (1983) containing, among other things, results of analyzing hair from residents of the communities of Glenwood, Hill Spring and Mountain View, near the Gulf and Shell plants.

The front-page story highlighted Snider's conclusion that concentrations of cadmium (Cd) and mercury (Hg) in hair were statistically correlated with living downwind from the plants and drew attention to the carcinogenic properties of Cd and Hg.

Dr. Snider defended his conclusions when he addressed the Task Force members at their third meeting on June 16, 1983.

Also at the third Task Force meeting, Dr. Thimm of the Energy Resources Conservation Board summarized the findings of an investigation by the University of Windsor (Gnyp and St. Pierre, 1983) of concentrations of metals in incinerator stack effluent from several sour gas plants, including those of Shell and Gulf.

According to the results of this study, the three most prevalent metals in the Gulf stack effluent, aluminum (Al), titanium (Ti) and iron (Fe), left the stack at rates of the order of 10 grams per hour. Cursory calculations show that these amounts are extremely small compared with amounts

present in the surrounding area. For example, the top inch of soil in one township receiving (hypothetically) all the effluent would accumulate only about 0.6 parts per million (ppm) extra Al, Ti and Fe in 25 years of continuous operation, which is insignificant compared with the levels of these elements found normally (1,000 to 50,000 ppm). Many elements are found in soil in much smaller concentrations, but the other elements found in stack effluent were emitted at much smaller rates than 10 g/h, so the amounts of these other elements are also insignificant, relative to their natural levels.

Dr. Thimm was quoted in an article in the June 21, 1983 edition of the Calgary Herald as saying that, at the rates of emission determined by Gnyp and St. Pierre (1983), no significant amount of any metal could have been ingested as a result of sour gas processing operations compared with amounts ingested from other, normal sources.

Need For Further Information

The technical members of the Task Force felt that, in view of the publicity attached to metal pollution, and consequent public concern, further work was required in order to support or refute the findings of Gnyp and St. Pierre (1983), and that direct measurements of metal concentrations at sites near the gas plants were required, rather than calculations based on assumptions. Measurements were required which were not subject to the accusation that the sour gas refining process could have been adjusted somehow before or during the period of measurement so as to affect the results (an

allegation made by some local residents). It was also recognized that the Shell plant emits roughly 10 times as much effluent as the Gulf plant did, and that no measurements were made by Gnyp and St. Pierre on effluent from the flare stacks at either plant.

WORK COMMISSIONED BY THE TASK FORCE

This section outlines the study of airborne pollution and other pollution studies and the rationale for the approach taken by the Task Force.

Airborne Pollution Studies

The studies of airborne pollution included taking samples of soil, litter, grass and lake sediment from near lakes at various distances up to about 15 km from the gas plants. These samples are often referred to below as the "lakeside samples", and were analyzed for a suite of metals.

In addition, garden vegetables were collected from residents living at various distances up to about 15km from the gas plants, and also analyzed for metals.

The soil, litter, grass, lake sediment and garden vegetable samples were also analyzed for $^{34}S:^{32}S$ ratios by Dr. Krouse of the Physics Department, University of Calgary.

Other Studies

Bullrush samples were taken, downslope from settling ponds at both sites and from three ponds at the Gulf site (there were no bullrushes at the Shell ponds). Bullrushes were also collected from Goose Lake, Dipping Vat Lake and Rouleau

Lake. All of these samples were analyzed for metals. In addition, sediment and water from the settling ponds at the Shell plant were collected and analyzed. Results of such analyses were already available for the Gulf plant.

Selenium concentrations were measured in three soil samples from the Gulf plant. These samples were taken from a point west of the process area, from a point east of the sulphur block and from the sulphur block run-off area.

Rationale

The technical members of the Task Force decided that accumulation of metals emitted by the gas plants might conceivably be detectable in grass, soil and lake sediment samples (but only if the results of Gnyp and St. Pierre were erroneously low). On the basis of three criteria, namely (i) concentration normally found in soil, (ii) concentration found in stack effluent and (iii) toxicity, the following suite of metals was decided on; arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn).

Since a series of lake waters was to be analyzed as part of the hydrogeological section of the Task Force's investigations, the technical members decided to obtain samples of lake sediment from these same lakes and to obtain grass and topsoil samples from near the shore of each lake (see Figure IV-1).

The other advantages of doing this were that the lakes are relatively easily located, both in the field and on a map; that the results are therefore easily plotted with no risk of error due to incorrect legal descriptions; and that the lakes

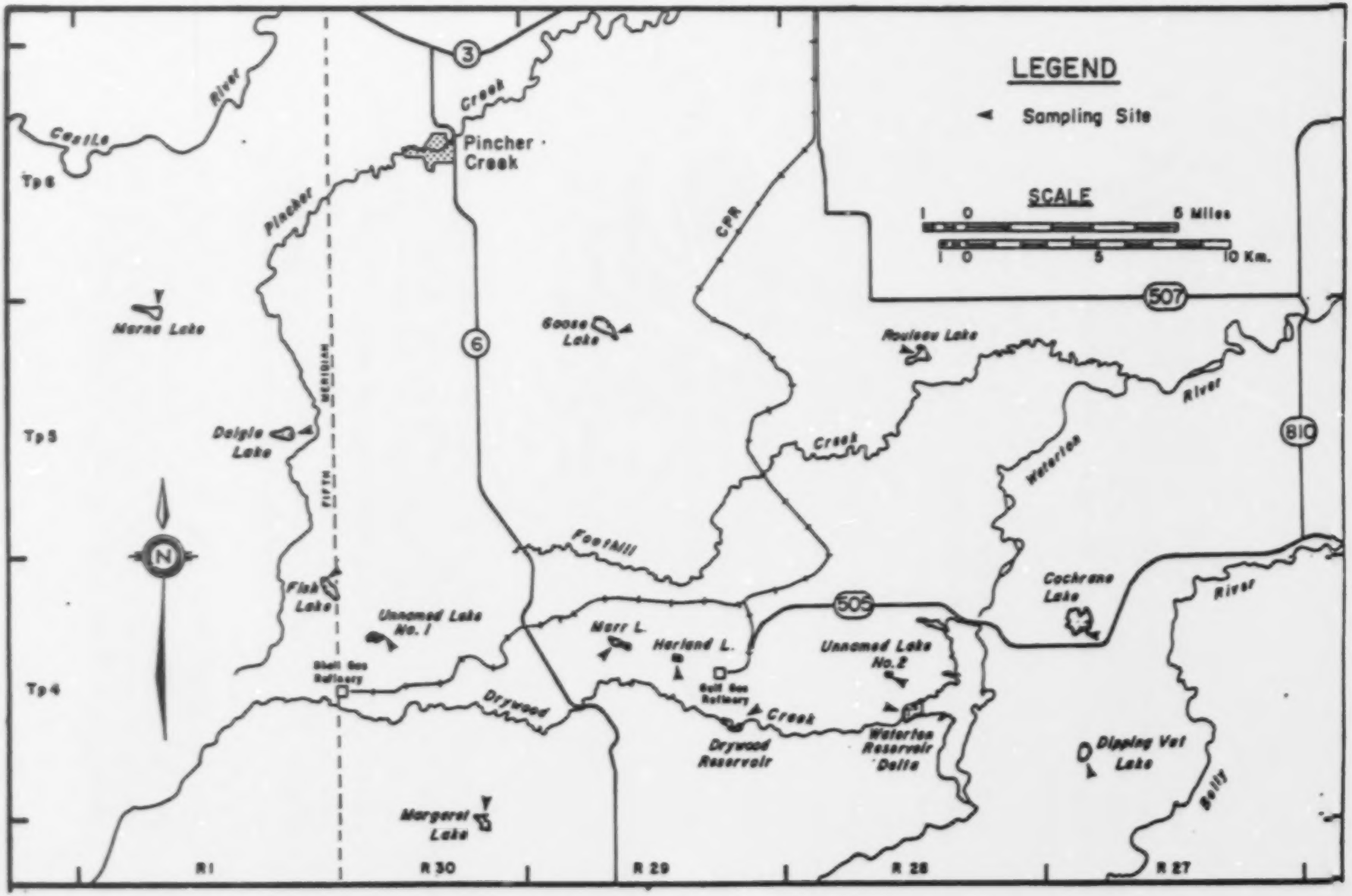


Figure IV-1. Location of Lakes and Sampling Sites Where Lake Sediment, Soil and Vegetation Samples were Collected.

Source: Hardy Associates Ltd., 1983, TASK FORCE.

are easily identified relative to other locations. Also, if future samples were requested, a direct comparison could be made with the present set of results, provided that the samples were analyzed for their total content of each element.

Extractable concentrations of the elements were not measured because of the likelihood of variations in soil type from site to site affecting the result, and because it is not easy to duplicate the exact conditions of extraction over an interval of time, should a future set of measurements be required.

Soil, litter and sediment samples were also analyzed for pH and electrical conductivity, to check for effects of air-borne pollution on these parameters.

Samples of potatoes and carrots were obtained in response to the suggestion that by eating home-grown vegetables, residents of the area might unwittingly be ingesting large quantities of some metals.

The reason for analyzing the "lakeside" samples and the vegetables for $^{34}S:^{32}S$ ratios was to obtain an estimate of the proportion of sulphur at each sampling site due to sour gas refining operations, either as a result of wind-blown sulphur dust from the sulphur block (for sites close to the plants) or because of air-borne plant sulphur arriving at the site by dry deposition or in precipitation.

This measurement is possible because sulphur in sour gas is enriched in the heavier isotope, compared with natural isotopic abundances of sulphur in Alberta (see below under "Principles of Stable Sulphur Isotope Studies) so that any

increase in $^{34}S:^{32}S$ ratios can be traced to sour gas processing.

The analysis of sediment, pond water and groundwater samples from the Shell plant was done in keeping with the terms of reference of the Task Force, in particular the requirement to investigate the possibility of sub-surface migration of toxic substances from the gas plant sites.

The analysis for selenium (Se) in three soil samples from the Gulf plant was done to examine the effect of soil pH on its selenium content. The question had been raised as to whether the presence of elemental sulphur in soil, or sulphur oxidation with accompanying decrease in pH, would suppress selenium uptake by plants and thereby induce selenium deficiency in grazing animals.

The analysis of bullrushes near the plants was done because such analyses might indicate metal contamination as a result of surface run-off. Bullrushes from distant lakes would give background metal concentrations.

The contribution of the community residents to our sampling rationale is gratefully acknowledged.

MATERIALS AND METHODS

The materials tested and a brief description of the methods of analysis and the principles underlying those methods are outlined below.

Sample Collection and Analysis

Grass, surface litter, topsoil (0-5 cm), samples of A, B and C soil horizons and lake sediment samples were collected

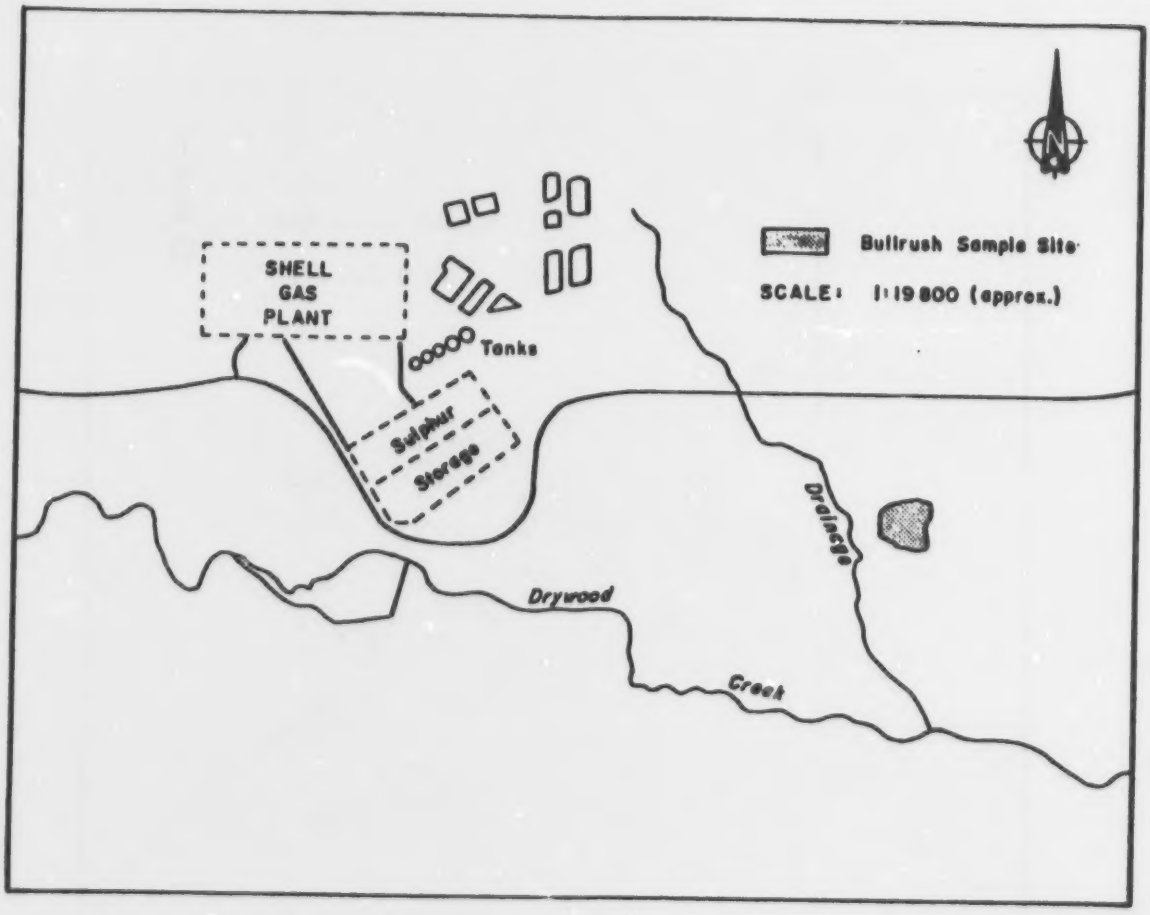
during August and September 1983 at the Gulf gas plant by Hardy Associates Ltd. The methods of sample collection are fully described in the report of Hardy Associates appended to this report (Appendix S-1). Briefly, grass samples were obtained by trimming existing vegetation from four 1 m^2 areas and discarding any leaves other than grass; samples of leaf litter (if present) were also taken. Soil samples were obtained by combining three cores (0-5 cm) from each area, or by trowel (soil horizons) after exposing the profile by digging.

Lake sediment samples were taken by dropping a vertical core sampler from a boat. Six core samples were bulked and a single representative sample sent for analysis.

The settling pond sediments at the Shell gas plant were obtained in similar fashion, on November 9, 1983. The surface run-off sludge storage pond, the aerobic digestion pond, the plant #2 slurry pond and ponds 2, 5, B, C, G and J were sampled; these ponds were considered to have borne the brunt of the effects of operating the Shell plant. At the same time, a sample of the water in each pond was collected. Bullrushes were collected in September and separated into tops and roots. The bullrushes were taken from points downslope from the Shell and Gulf settling ponds, from Gulf pond 7 and from un-numbered ponds near ponds 6 and 8 (see Figure IV-2 and IV-3 for sampling areas).

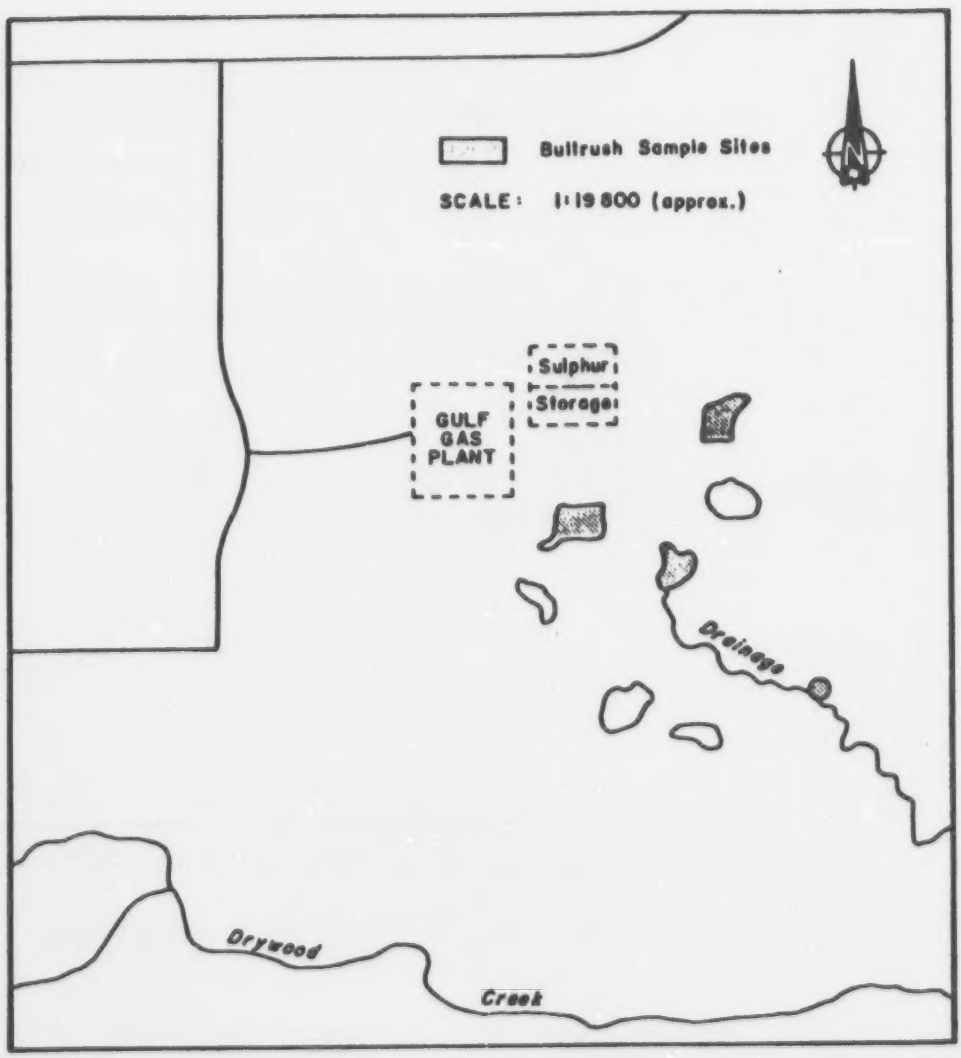
Garden vegetables (potatoes and/or carrots were chosen for ease of sampling and storage) were obtained from 26 local residents living at various distances from the gas plants by Mr. R. Lyons, the District Agriculturist.

Figure IV-2. Sketch of Shell Gas Plant Showing Location Where Bullrush Sample Was Collected.



Source: Hardy Associates Ltd., 1983, TASK FORCE.

Figure IV-3. Sketch of Gulf Gas Plant Showing Locations Where Bullrush Samples Were Collected.



Source: Hardy Associates Ltd., 1983, TASK FORCE.

A complete array of samples, except for the samples of soil horizons, was sent to the Saskatchewan Research Council (SRC) laboratory for analysis.

A second complete array of samples, except for settling pond sediment cores, was sent to the Physics Department, University of Calgary, for sulphur isotope analysis.

A set of four grass and four (0-5 cm) soil samples from near Fish Lake were sent for analysis to Norwest Labs (NWL) in Edmonton as a check on the SRC results.

Groundwater samples were taken in June, 1984 (by staff from Monenco Ltd.) from five shallow piezometers near the periphery of the Shell plant (installed by Monenco Ltd. in 1983). A water sample was also taken from a natural spring 1 km west of the Shell reservoir on Drywood Creek. All samples were sent to Envirotest Labs. in Edmonton for analysis for organic compounds by gas chromatography.

Elemental sulphur samples were taken directly from sulphur blocks at the gas plants.

Atmosphere Sampling

High volume sampling of the atmosphere at ground level (Riviere site) was done using multiple filter techniques developed by Forrest and Newman (1973). Particulate matter was first collected on a glass filter and SO_2 was then trapped by reaction with a cellulose filter treated with KOH-triethanolamine (TEA). A second KOH-TEA treated filter paper was used as a backup to trap SO_2 which eluded the first paper.

Analysis for Metals

Soils and sediments were digested with an $HCl/HNO_3/HClO_4$ mixture and analyzed by ICP. Some samples were later digested using HF also before analyzing for lead (Pb) by ICP; this improved recovery of Pb. Vegetation was digested with a 4:1 mixture of HNO_3 and $HClO_3$ before ICP analysis.

Arsenic and selenium were determined by AA spectroscopy after hydride generation. Mercury was determined by AA using a cold vapour technique.

Full details of these procedures are available from the Saskatchewan Research Council.

Principles of Stable Sulphur Isotope Studies*

Isotopes are atomic species of an element which differ in the number of neutrons in their nuclei and hence their masses.

Since many processes are mass dependent, isotope abundances are altered in nature. By measuring isotope abundance variations, one obtains information about the past history of a sample.

Sulphur, element 16, has four stable isotopes - ^{32}S, ^{33}S, ^{34}S and ^{36}S - with average terrestrial abundances of 95, 0.7, 4 and 0.2 percent, respectively. Stable Isotope Relative Abundance (SIRA) determinations for sulphur are usually restricted to ^{32}S and ^{34}S because of their high concentrations. In this case, a $\delta^{34}S$ scale is defined as:

* The information here and on pages 61 to 64 was contributed by Dr. R. Krouse, University of Calgary.

$$\delta^{34}S \text{ in } {}^{o}/_{oo} = \left[\frac{[{}^{34}S/{}^{32}S]_X}{[{}^{34}S/{}^{32}S]_S} - 1 \right] \times 10^3 \qquad \ldots(IV\text{-}1)$$

where $^{o}/_{oo}$ is parts per thousand (per mil) and $[^{34}S/^{32}S]$ is the ratio of the number of ^{34}S to ^{32}S atoms in the specimen. "X" is the sample, whereas "S" is a standard used internationally, troilite (FeS) from the Canon Diablo meteorite.

Positive and negative $\delta^{34}S$ values mean that the sample is "enriched" and "depleted", respectively, in comparison with the standard. Deep-seated sulphur in the earth's crust tends to be close to the meteorite reference. Materials which range widely in their sulphur isotope composition are likely to have participated in oxidation/reduction reactions in the bacterial sulphur cycle. The current oceans are enriched in ^{34}S with $\delta^{34}S$ values near +21 $^{o}/_{oo}$. There is evidence from evaporite studies that the $\delta^{34}S$ values of oceanic sulphate have fluctuated between +10 $^{o}/_{oo}$ and +35 $^{o}/_{oo}$ over geological time.

Of particular relevance to this study is that H_2S in deep sour gas occurrences has been derived from evaporite sulphate by thermochemical conversions which were accompanied by minimal isotopic fractionation. Hence sour gas has quite positive $\delta^{34}S$ values and SO_2 emitted during gas processing is similarly enriched in ^{34}S.

Soils and vegetation in non-industrial areas of Alberta have $\delta^{34}S$ values ranging from 0 down to -30 $^{o}/_{oo}$. The latter are identified with Cretaceous shale outcroppings in the Peace River area.

Therefore, in Alberta, the difference in isotopic composition of sulphurous emissions and environmental receptors has proved effective in tracing the fate of atmospheric pollutants. Successful tracing requires that isotopic fractionation is not extensive. Fortunately, the oxidation of H_2S to SO_2 in incinerators and atmospheric oxidation of SO_2 to sulphate are accompanied by minimal sulphur isotope fractionation. Similarly, isotope selectivity during assimilation of SO_2 and sulphate by vegetation is very small.

PREPARATION OF SAMPLES FOR SULPHUR ISOTOPE ANALYSIS

In the laboratory, the filters with the particulate samples were treated with an HCl-H_3PO_2-HI reduction mixture in a distillation apparatus. The generated hydrogen sulphide was trapped as cadmium sulphide and subsequently converted to silver sulphide by the addition of 0.IN silver nitrate. This silver sulphide contained all the sulphur present in samples of particulate matter collected according to their size class. In some instances where insufficient sulphur was present in one size class of particulate matter, the sample was combined with that from the next size class.

The TEA-KOH filters were washed with de-ionized, double-distilled water and the washings oxidized by the addition of hydrogen peroxide to ensure conversion of all sulphur species to sulphate. The sulphate was precipitated as $BaSO_4$ by the addition of hot 0.IN $BaCl_2$. The $BaSO_4$ was treated with a HCl-HI-H_3PO_2 reduction mixture to generate H_2S which was converted to Ag_2S as described previously.

Elemental sulphur was placed with excess silver powder in an ampoule which was evacuated, sealed, and then heated to produce Ag_2S.

Sulphur Dioxide Preparation

The prepared Ag_2S (up to 20 mg) was thoroughly mixed (1:4 by wt) with Cu_2O, and packed into a 0.5 cm x 3 cm quartz tube. This tube was inserted into the SO_2 preparation line which was then evacuated. After 10 min evacuation, a valve leading to vacuum was closed and the quartz tube containing the Ag_2S-Cu_2O moved by a magnetic pushrod into a furnace maintained at 900°C. Sulphur dioxide generated from the thermochemical reaction was frozen in liquid nitrogen and then pumped to remove O_2. Minute quantities of H_2O and CO_2 are also produced in these conversions. The H_2O was removed by passing the gases through a trap cooled by a dry ice-acetone bath, while CO_2, because of its higher vapour pressure, was removed by a vacuum distillation from a trap cooled by a n-pentane bath (the pentane was cooled down to its solidification point by adding liquid nitrogen). After these procedures, the SO_2 was ready for isotopic analysis.

Total sulphur in soil was converted to sulphate by oxidation using either a Parr Bomb or a HNO_3-Br_2 mixture (volume ratio 5:1). For the latter, the solution (15 ml oxidant mixture to estimated $BaSO_4$ equivalent of 200 mg) stood overnight at room temperature and was gently heated on a steam bath the next day to evolve Br_2. After heating to dryness, 10 ml of concentrated HCl were added and the sample evaporated to dryness again. This process was repeated. Finally, the sample was dissolved in 25 ml H_2O with 2 ml

HCl. This solution (or Parr Bomb washings) was filtered and $BaSO_4$ precipitated by the addition of boiling 10 percent $BaCl_2$ solution.

The $BaSO_4$ was then reduced to H_2S in a reflux column using a $HCl-HI-H_3PO_2$ mixture. The H_2S was precipitated as CdS and converted to Ag_2S which was in turn oxidized to SO_2 for sulphur isotope analyses in a stable isotope mass spectrometer.

Samples of raw gas from each plant were treated with cadmium acetate to precipitate CdS which was then similarly converted to SO_2.

Mass Spectrometry

The SO_2 was introduced to the mass spectrometer directly from the preparation line through a magnetic valve system which alternatively switches between a reference SO_2 sample and the one which has just been prepared. The mass spectrometer has been built around a Micromass 602 analyzer. Ion currents of mass 64 and 66 were digitized and passed to an AIM65 micro-computer which calculated the $\delta^{34}S$ value after corrections were made for oxygen isotope composition at mass 66 ($^{32}S^{16}O^{18}O$) and ($^{34}S^{16}O_2$).

RESULTS AND DISCUSSION

The results of our studies of airborne pollution and other studies are outlined below.

Airborne Pollution Studies

This section contains the results of analyzing lakeside samples and vegetables for metals and sulphur isotopes.

1. Metals in "Lakeside" Samples

   The results of analyzing the grass, litter, topsoil and sediment samples from near the various lakes are given in full in the report by Hardy Associates appended to this report (Appendix S-1).

   A summary of these results is presented in Figure IV-4, which shows the concentration of metals in grass (topmost set of figures), litter (next set down), soil (next set down) and lake sediment (bottom set of figures). The results obtained by NWL (see Appendix S-1) for the Fish Lake set of soil samples were in reasonable agreement with the SRC results shown in Figure IV-4.

   After repeated analyses, discrepancies still existed between the results obtained by NWL and the SRC for cadmium and lead in the set of grass samples from Fish Lake. The NWL results were more than five times greater than the SRC results. The results for Cd and Pb in grass (and also in surface litter, analyzed similarly) shown in Figure IV-4 should therefore be treated with caution.

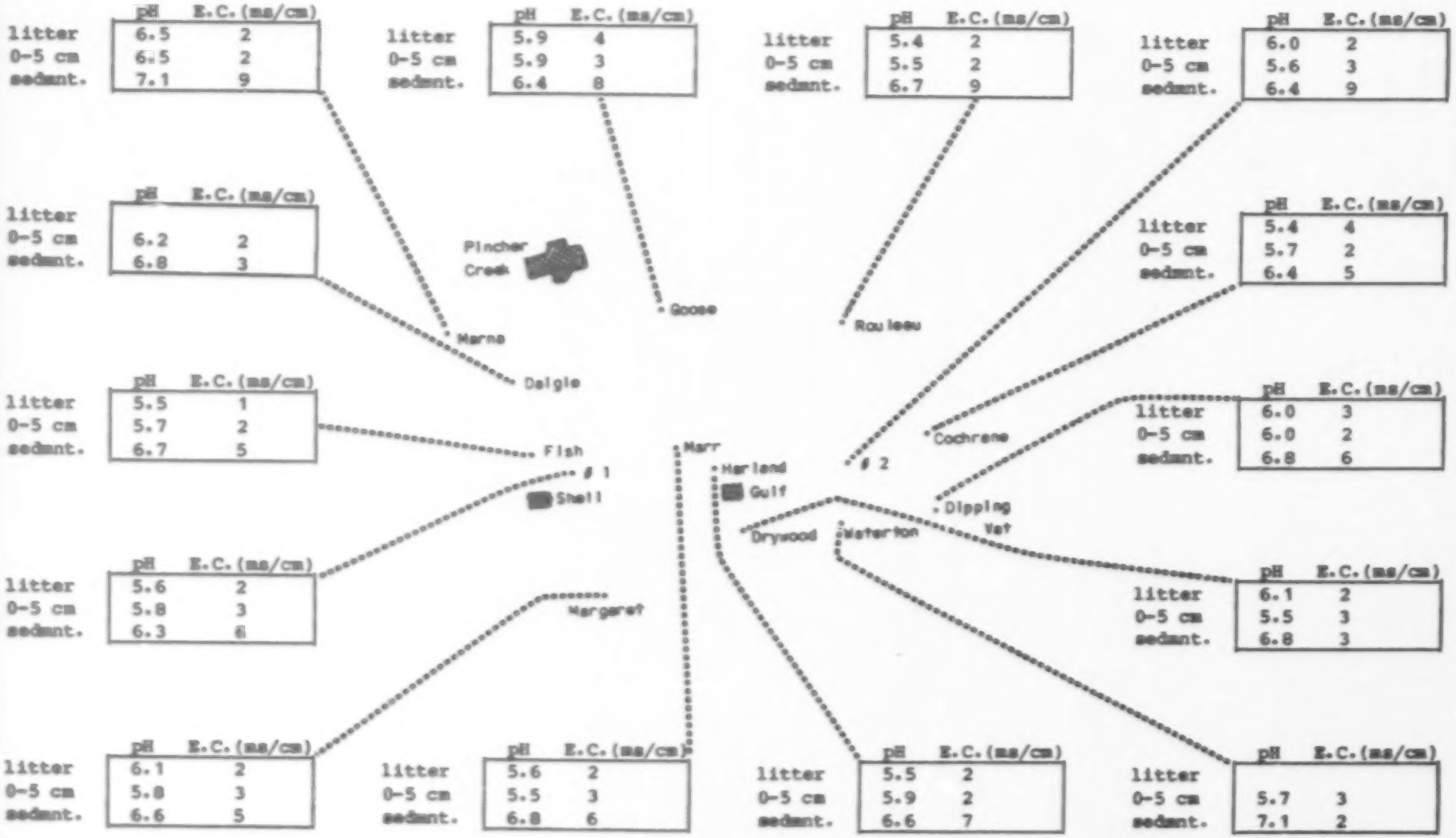
   The results of analyzing surface litter, soil and lake sediment for pH and electrical conductivity (EC) are shown in Figure IV-5.

Figure IV-4. Concentration of Metals in Grass, Surface Litter, Topsoil (0 - 5cm) and Lake Sediment.

* Result was below detectable limits.

Source: Hardy Associates Ltd., 1983, TASK FORCE.

FIGURE IV-5 pH and ELECTRICAL CONDUCTIVITY OF LITTER, TOPSOIL and SEDIMENT SAMPLES from the TWIN BUTTE AREA



Source: Saskatchewan Research Council, 1983, TASK FORCE.

There is no discernible trend in the results shown in Figure IV-4 and IV-5 with point of origin, or proximity to the sour gas plants. This finding is consistent with the results obtained by Gnyp and St. Pierre (1983) and refutes the suggestion that any substantial deposition of the metals analyzed for has occurred as a result of aerial transport from the sites of sour gas processing operations.

The results shown in Figure IV-4 can be compared with the average concentrations for soil and grass given in Table IV-1.

This comparison indicates that "lakeside" grass contained on average smaller concentrations of the metals analyzed for than are usually found in grass. Concentrations of metals in the corresponding soil samples were roughly equal, within a factor of 2 or 3, to those normally found in soil.

Selenium levels in the grass samples were below the detectable limit of 0.04 ppm in five of the fourteen cases. The average for the remainder was 0.12 ppm, with the highest value being 0.3 ppm. These results suggest that a selenium deficiency exists in certain areas where samples were taken.

2. S Isotopes in "Lakeside" Samples

This summary is, at the time of writing, the only existing report of Dr. Krouse's results. It was reviewed by Dr. Krouse before the final draft was produced.

Results of measuring ^{34}S values of elemental sulphur from the sulphur block at the Gulf plant;

TABLE IV-1
Concentrations of Chemical Elements in Soils and Grass (ppm)

Element	Soil On Glacial Till	Grass (dry wt. basis)
As	7	0.3
Be	2	<0.1
Cd	0.5	0.2
Cr	80	0.2
Cu	20	10
Hg	0.05	0.02
Ni	20	1
Pb	20	2
Se	0.4	0.1
Zn	60	30

Source: Reference data used by Norwest Soil Research Ltd. based largely on data given by Pendias & Pendias in "Trace Elements in Soils and Plants" (CRC Press, 1984). Some values privately communicated to J. Ashworth. The values are averages and can be multiplied or divided by a factor of up to 2 or even 3 in some cases to get the likely range encountered naturally. TASK FORCE.

of untreated sour gas ("raw" gas) from the Gulf plant and from the two separate "sheets" processed by the Shell plant, and of atmospheric samples of particulate material and of air filters exposed for approximately one day downwind from the Shell plant are given in Table IV-2.

These results show that windblown elemental sulphur and other forms of air-borne sulphur from the gas plants have strongly positive $\delta^{34}S$ values in the range 16-25.

These figures can be compared with the average results of measuring $\delta^{34}S$ for sulphur extracted from grass (Figure IV-6), litter (Figure IV-7), surface soil (Figure IV-8), the A horizon of soil (Figure IV-9), the B horizon of soil (Figure IV-10) and lake sediment samples (Figure IV-11) obtained as previously described. Complete results are in Appendix S-2.

3. Isotope Ratios in Soil and Sediment Samples

In general, the values found range from around zero in topsoil samples taken from sites near the Drywood Creek Valley which connects the Shell and Gulf plants, and fall to more negative values at sites further away, with the most negative value being found at Marna Lake, 16 km northwest of the Shell plant (Figure IV-8).

Values of $\delta^{34}S$ in successively deeper soil horizons follow the same general pattern but tended

Table IV-2

$\delta^{34}S$ Values (calculated using Equation IV-1) in Elemental Sulphur and Raw Gas from the Gulf and Shell Plants, and in Particulate Sulphur and SO_2 Extracted from the Atmosphere

Source of Sulphur	$\delta^{34}S$ (per mil)
ELEMENTAL SULPHUR	
- Shell	+17.0, +17.1
- Gulf	+18.1, +18.2, +18.3
RAW GAS	
- Shell (sheet 3)	+16.4
- Shell (sheet 4)	+16.3
- Gulf	+17.3
ATMOSPHERE (~24 H PERIOD IN OCT. 1983)*	
- Particles captured on glass filter	+19.7, +21.6, +15.8
- SO_2 trap #1	+21.3, +16.5, +16.4
- SO_2 trap #2	+25.0, +22.9, +20.7

*mg S trapped were <2, 40-90 and 6-11 mg on the 3 traps.

Source: Krouse, University of Calgary, 1984, TASK FORCE.

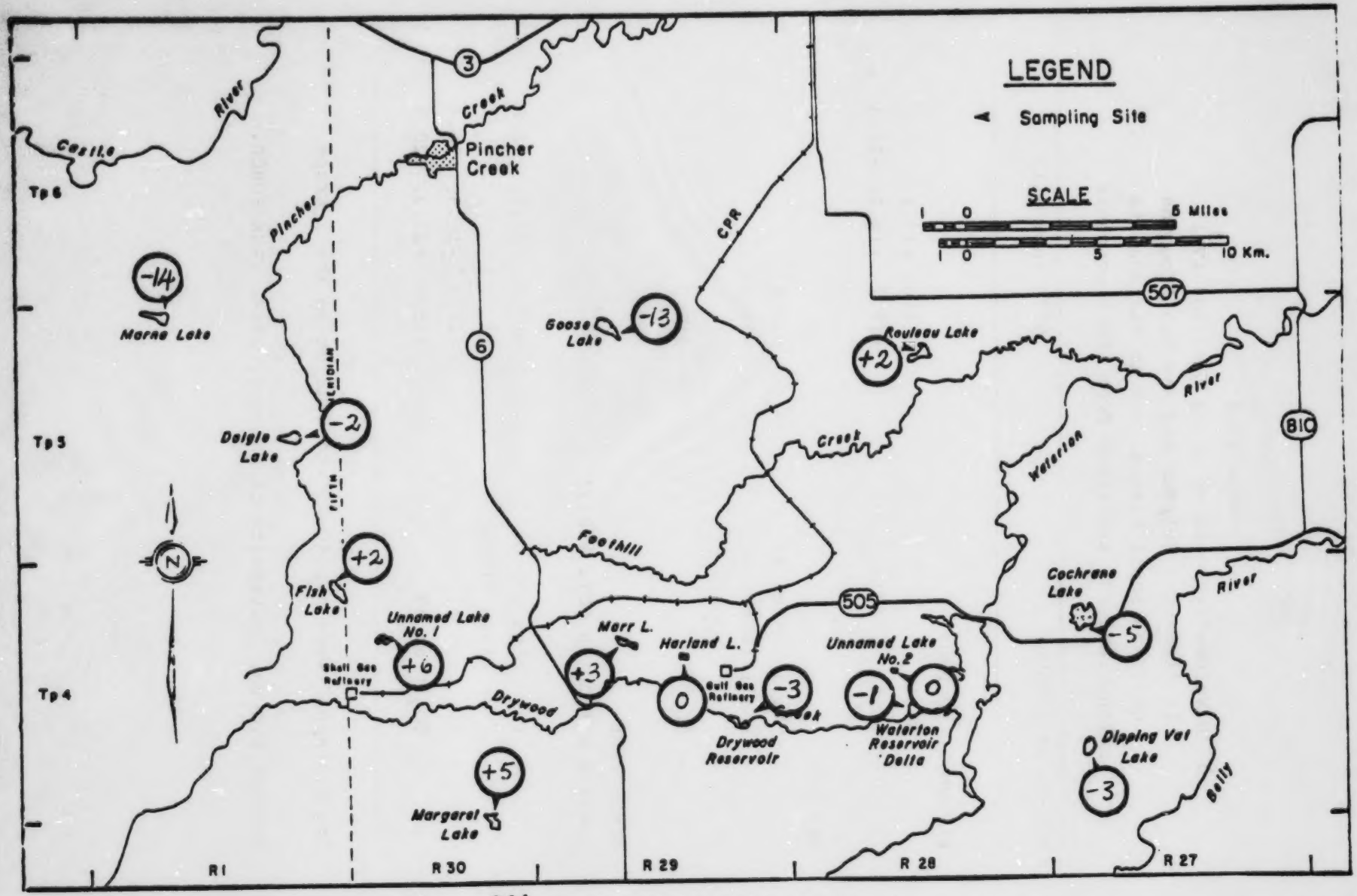


Figure IV-6. $\delta^{34}S$ Values in Lakeside Grass

Source: Krouse, University of Calgary, 1984, TASK FORCE.

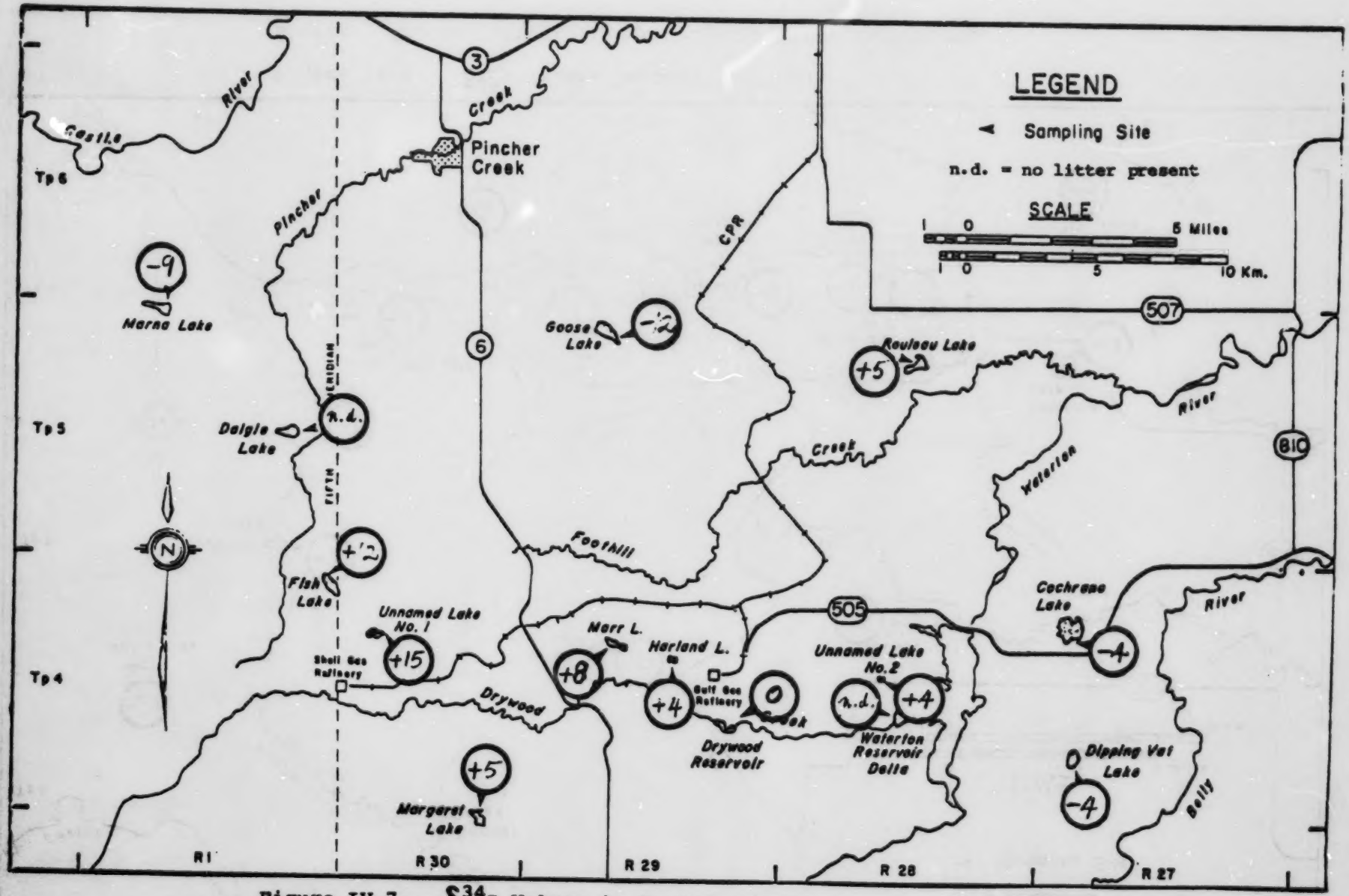


Figure IV-7. $\delta^{34}S$ Values in Surface Litter

Source: Krouse, University of Calgary, 1984, TASK FORCE.

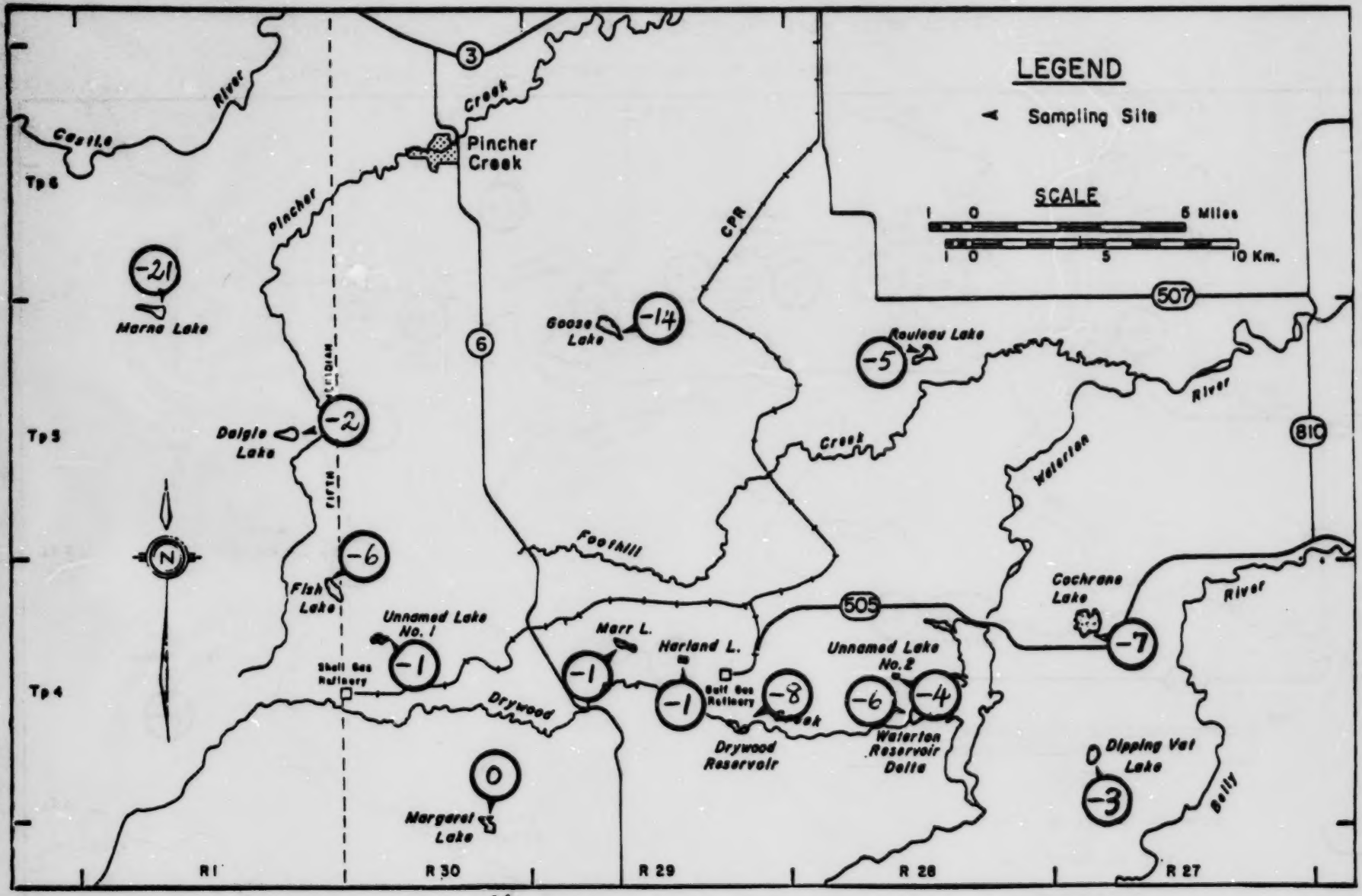


Figure IV-8. $\delta^{34}S$ Values in Soil (0-5 cm).

Source: Krouse, University of Calgary, 1984, TASK FORCE.

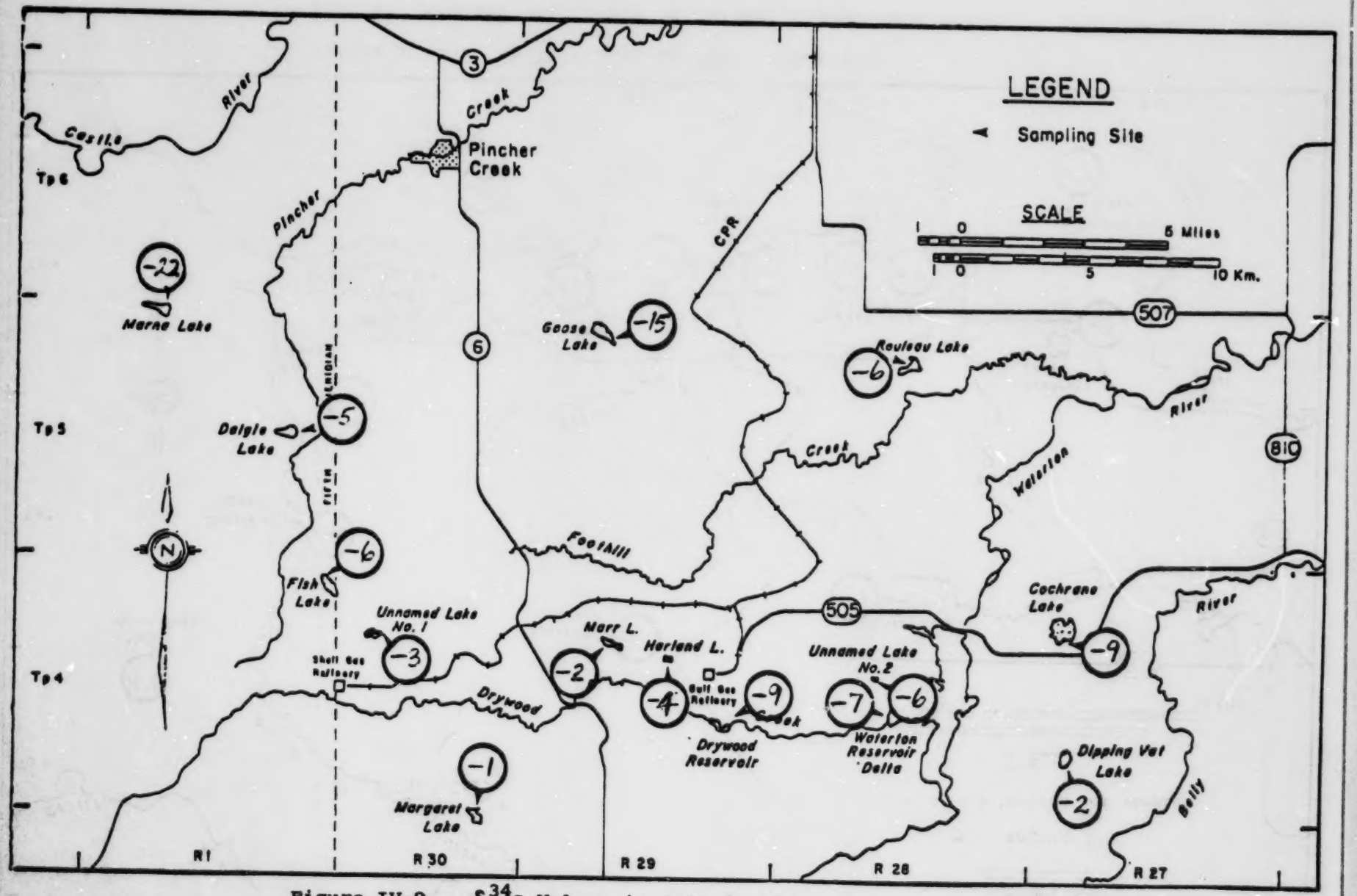


Figure IV-9. $\delta^{34}S$ Values in Soil (A Horizon).

Source: Krouse, University of Calgary, 1984, TASK FORCE.

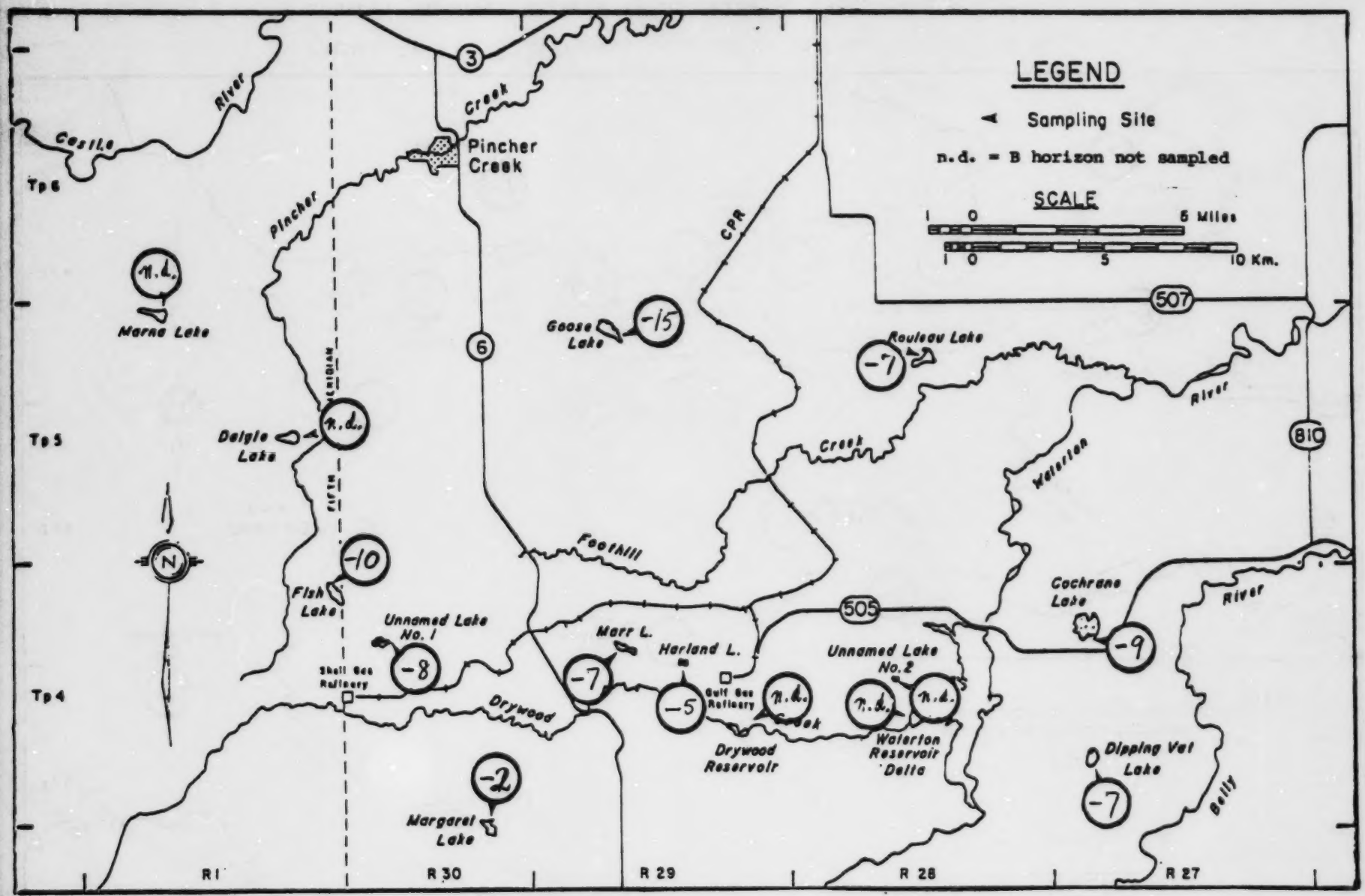


Figure IV-10. $\delta^{34}S$ Values in Soil (B Horizon).

Source: Krouse, University of Calgary, 1984, TASK FORCE.

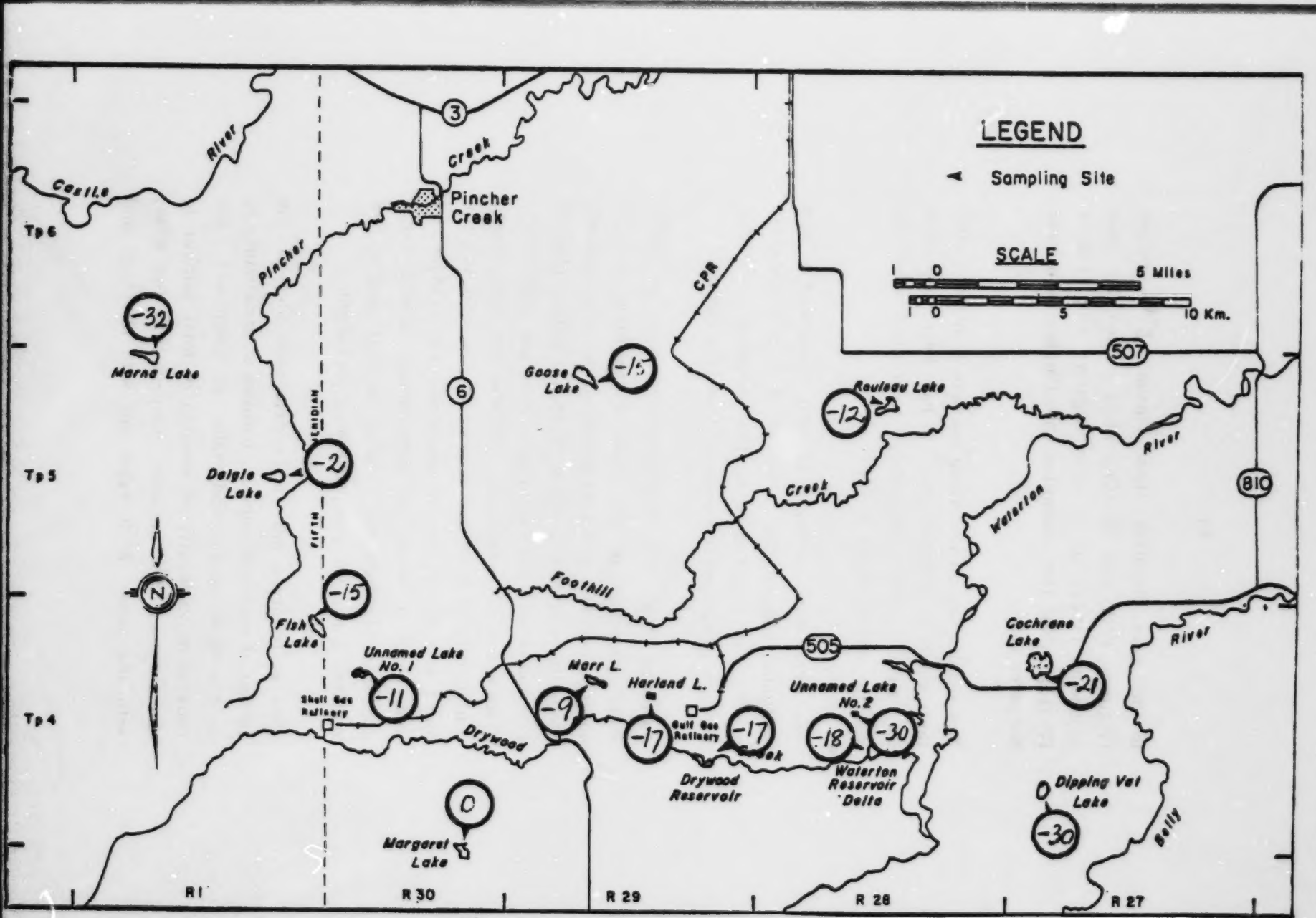


Figure IV-11. $\delta^{34}S$ Values in Lake Sediment.

Source: Krouse, University of Calgary, 1984, TASK FORCE.

to be more negative than topsoil $\delta^{34}S$ values (Figures IV-9 and IV-10), while values for lake sediments tended to be more negative still (Figure IV-11), with the exception of Daigle Lake and Margaret Lake.

The results are on the whole consistent with the view that sulphur enriched in ^{34}S has been deposited on sites where originally, naturally occurring sulphur was depleted in ^{34}S.

The much more strongly negative results for lake sediments suggest that a source of sulphur depleted in ^{34}S has supplied S to the sediments, possibly through groundwater movement into lake basins.

Assuming that the "background" value of $\delta^{34}S$ found naturally in the Twin Butte area, in the absence of industrial contamination, is approximately minus 20, and that a value of approximately plus 20 represents 100% derivation from sour gas processing, a scale can be established whereby the approximate contribution of sour gas sulphur to the total sulphur found in a sample can be estimated. For example, on this basis a value of zero would indicate that approximately half the sulphur in that sample had resulted from sour gas processing operations.

This scale gives only an approximate idea of the amount of sour gas sulphur, because of uncertainty as to the true background value of each site, and because of variability in amounts of total sulphur in the samples. For instance, samples from two sites, with the same $\delta^{34}S$ value but with one high and

one low in total S to begin with, that then received equal amounts of sour gas sulphur would have different $\delta^{34}S$ values, the first sample coming out lower than the second.

However, total sulphur in the samples (see Appendix S-2) did not vary by more than about 30% from the mean value for the same type of sample, so the scale is reasonably reliable.

Another cause of uncertainty in interpreting the results is the continual cycling of sulphur in the environment. Some of the sour gas sulphur deposited at a site will in time be lost from that site as gases produced by biological oxidation and reduction processes. It is not known whether the measured values represent an equilibrium that has been established since sour gas processing began, or whether the observed values will become more positive before reaching equilibrium.

It can be seen (Figures IV-8, 9 and 11) that the $\delta^{34}S$ results for soil and sediment from Daigle Lake are more positive than the results for Fish Lake which is actually the closer to the Shell plant of the two lakes. Variability in the background level of ^{34}S is probably responsible for this result, and for the results obtained at Margaret Lake.

Values of $\delta^{34}S$ in grass were more positive than values in topsoil and values in surface litter were more positive still. Grass, and particularly surface litter, therefore seem to be good indicators of deposition of sulphur from the gas plants. Some

SO_2 may be sorbed on litter more than on living plant material and thereby increase the proportion of ^{34}S.

4. Implications of the Sulphur Isotope Results

A good indicator of the intensity of deposition of sour gas sulphur at a site may be the value of $\delta^{34}S$ in grass or surface litter (judging from the more positive values obtained for these materials) relative to the value in the soil A horizon (which is not likely to have been enriched in ^{34}S-depleted material carried by groundwater). Viewed in this way, clear trends are apparent in the ^{34}S results, which indicate that there is (1) a zone of relatively intense deposition of air-borne sulphur from the gas processing plants, in the direction of Drywood Creek Valley at least as far as the Waterton Reservoir (2) another such zone in the direction of the Pincher Creek valley at least as far as Daigle Lake, and (3) possibly another zone in the direction of the Foothills Creek valley as far as Rouleau Lake.

The air-borne sulphur (presumably SO_2 for the most part) may actually follow these valleys, but more detailed sampling would be required to confirm this hypothesis.

Since any pollution by metals emitted from the gas refineries would follow a similar trend to that observed for air-borne sulphur it follows that, in the absence of any discernible trend in concentrations of metals with distance and orientation of the sampling sites from the gas

plants, the amounts of these air-borne metals are insignificant compared with amounts present naturally.

5. Metals in Potatoes and Carrots

The potatoes and carrots submitted by residents were also analyzed by the SRC for the range of elements for which they normally analyze food samples, which is more comprehensive than the suite of metals looked for in the lakeside samples discussed above (see Appendix S-3). The largest concentration of each element found, and a set of results for the "average" potato or carrot have been listed in Table IV-3 together with the "average" daily intake of each element in our food. Only one significant figure is given with these "averages" but a footnote to Table IV-3 explains that a range of values is implied.

These "average" values were obtained from "Guidelines for Canadian Drinking Water Standards" (1978, Supporting Documentation), "Trace Elements in Human and Animal Nutrition" by J. Underwood (Academic Press, 1977), "Nutrition; Macronutrients and Nutrient Elements" by G. H. Beaton and E. W. McHenry (Academic Press, 1964) and by consultation and correspondence with staff at the Foods and Nutrition Dept., University of Alberta, and at the Food Directorate, Health and Welfare Canada, Ottawa.

Compared with this reference data, the data for the residents' vegetables show that only chromium (Cr) and manganese (Mn) were found in conceivably greater-than-average concentrations is some of the potatoes and carrots. Some of the vegetables submitted were

TABLE IV-3 Metals in Vegetables from the Twin Butte area and Daily Intake of Chemical Elements

Element		Largest Concentration in Samples from Mr. Lyons (mg/kg)		Average Concentration Found Normally (mg/kg)		Daily Intake of Each Element From an Average Adult Diet (mg)
		Potatoes	Carrots	Potatoes	Carrots	
Aluminum	(Al)	8.7	4.4	(2)	(2)	20
Arsenic	(As)	<0.01	<0.01	(0.08)	(0.08)	0.2
Barium	(Ba)	8.2	7.1	(2)	(2)	1
Beryllium	(Be)	<0.03	<0.03	-	-	-
Boron	(B)	1.9	3.0	2	(1)	3
Cadmium	(Cd)	0.13	0.08	(0.06)	(0.06)	0.07
Calcium	(Ca)	140	460	100	400	1,000
Cobalt	(Co)	<0.03	<0.03	(0.01)	(0.01)	0.1
Copper	(Cu)	2.2	0.82	2	1	2
Chromium	(Cr)	0.29	0.35	0.05	(0.1)	0.2
Iron	(Fe)	10	6.0	10	9	20
Lead	(Pb)	0.2	0.2	0.05	0.1	0.2
Magnesium	(Mg)	340	310	300	200	300
Manganese	(Mn)	11	18	4	4	4
Mercury	(Hg)	0.01	0.07	0.002	0.002	0.01
Molybdenum	(Mo)	0.60	0.10	0.3	0.6	1
Nickel	(Ni)	0.39	0.22	(0.04)	(0.04)	0.4
Phosphorus	(P)	1,000	550	500	400	2,000
Potassium	(K)	7,200	4,400	5,000	3,000	3,000
Selenium	(Se)	<0.02	<0.02	-	-	0.2
Silver	(Ag)	<0.03	<0.03	-	-	0.1
Sodium	(Na)	79	970	300	500	4,000
Titanium	(Ti)	0.08	0.06	(0.04)	(0.04)	0.4
Tungsten	(W)	<0.1	<0.1	-	-	-
Vanadium	(V)	<0.2	<0.2	(<0.01)	<0.01	0.3
Zinc	(Zn)	7.2	3.4	4	2	20

Concentrations are given in milligrams of each element per kilogram of fresh vegetable. The symbol <means "less than" the detectable limit given.
The numbers in the last three columns are very approximate estimates, due to natural variability. Divide or multiply each one by a factor of 4 or 5 to get the likely range. For example, 5 would indicate anywhere between 1 or 2 mg and perhaps 20 or 25 mg.
Numbers in parentheses are based on results for other vegetables and may be even less precise.

Source: Saskatchewan Research Council, 1983, TASK FORCE.

very small in size, which tends to increase the concentration of the elements they contain.

Four separate growers supplied the sets of vegetables with the highest concentrations of Cr and Mn, so there is no obvious link between these metals and the source of the vegetables. The normal dietary intake of potatoes is 190 g/day and of carrots is 50 g/day, according to Kirkpatrick and Coffin (1977). Eating ordinary servings of even these metal-rich vegetables would therefore supply only a portion of the normal daily intake of the elements they contain.

There were no trends in the results when viewed in relation to the source of the samples (see Appendix S-3). For example, chromium concentrations in carrots (Figure IV-12) were below detectable limits except at seven sites whose location is not consistent with Cr having been carried there on the wind; other sites "downwind" (east - northeast) from the gas plants had no detectable Cr. Zinc concentrations in potatoes (Figure IV-13) varied from about 2 to about 7 ppm, independently of the point of origin of the samples. Cadmium concentrations in potatoes (Figure IV-14) were highest in samples taken from sites near Goose and Rouleau Lakes, more than 10 km from the gas plants.

Selenium concentrations in the vegetables were less than 0.02 ppm; however, potatoes and carrots do not normally accumulate selenium (see Reference #17, Chapter V).

The implications of these results are that there is no sign that sour gas processing operations have

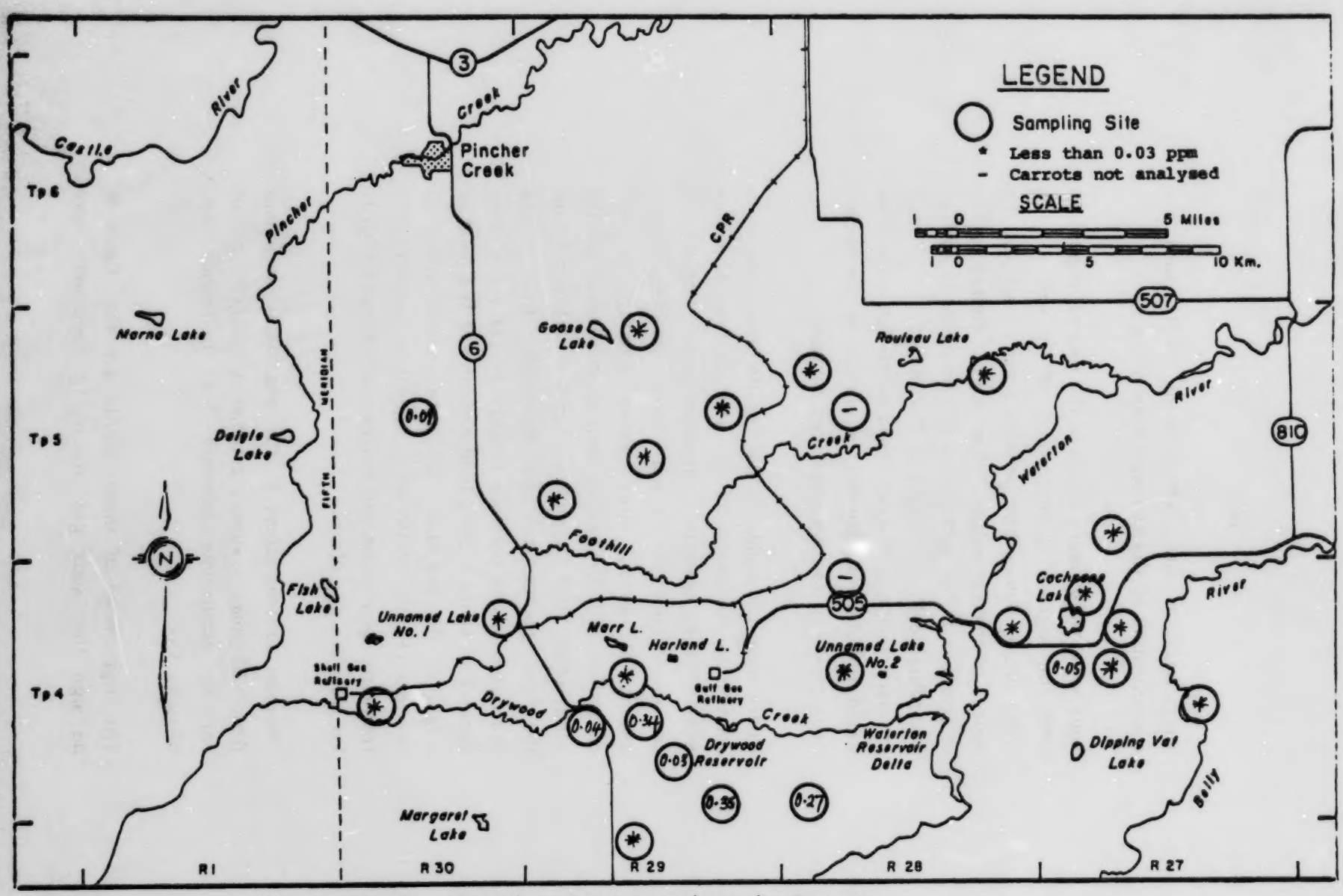


Figure IV-12. Chromium Concentrations in Carrots.

Source: Saskatchewan Research Council, 1983, TASK FORCE.

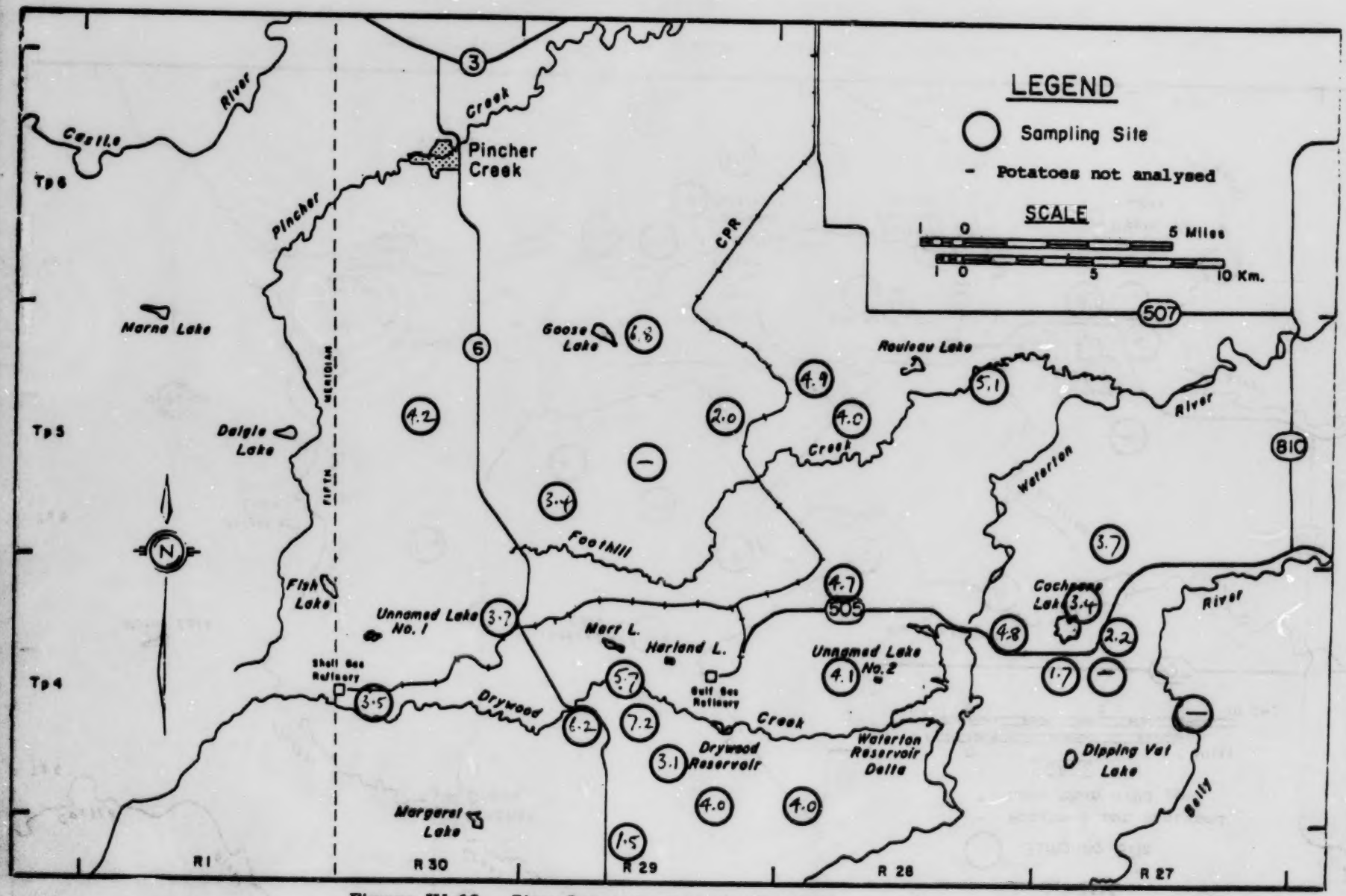


Figure IV-13. Zinc Concentrations in Potatoes.

Source: Saskatchewan Research Council, 1983, TASK FORCE.

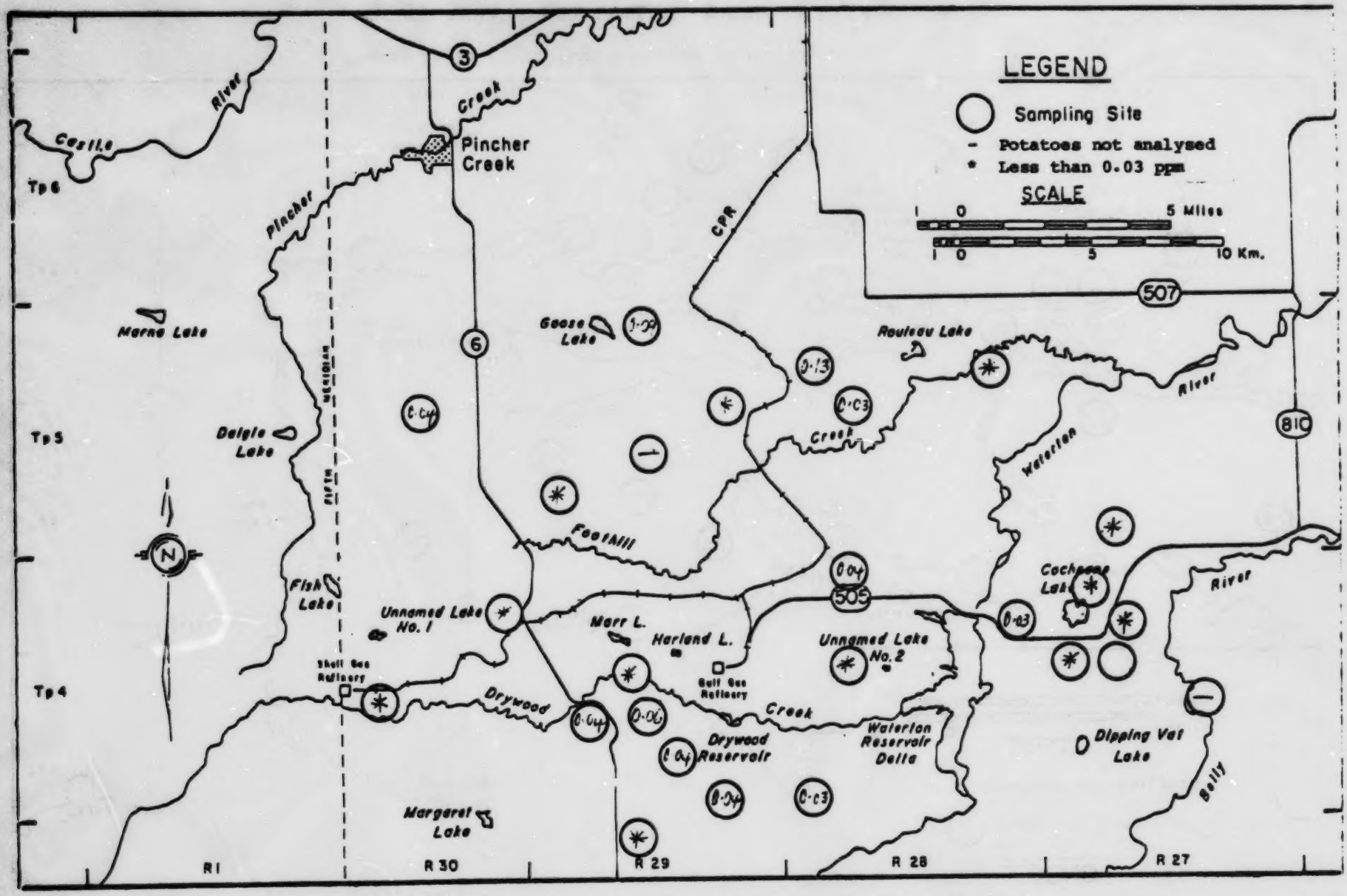


FIGURE IV-14. Cadmium Concentrations in Potatoes.

Source: Saskatchewan Research Council, 1983, TASK FORCE.

affected concentrations of any element analyzed for, and that the vegetables sampled could not provide a dangerously large amount of any of these elements, when included in the diet.

6. S Isotopes in Vegetables

The $\delta^{34}S$ values for the potatoes and carrots submitted by local residents to the District Agriculturist generally followed the trend described above for "lakeside" samples, in that the most positive values were observed for the most part at sites near the valley of Drywood Creek (Figures IV-15 and 16).

However, there were notable exceptions to this general rule, for example values ranging from minus 5 to plus 3 at two sites on either side of Highway #6, about 14 km north of Drywood Creek.

These values are inconsistent with the values of approximately minus 13 obtained for "lakeside" samples from Goose Lake. A likely explanation for the inconsistency lies in the fact that fertilizers such as ammonium phosphate sulphate (16-20-10), ammonium sulphate (21-0-0) and ammonium phosphate (11-48-0 or 11-55-0) contain sulphur which is likely to be enriched in ^{34}S, because sulphuric acid made from sour gas sulphur is used by several major fertilizer manufacturers in western Canada to extract phosphate rock. If these fertilizers have at some time been applied to the gardens producing the vegetables which were analyzed, a more positive value would be obtained for those vegetables.

Consistently more positive values of $\delta^{34}S$ were obtained for carrots than for potatoes from the same

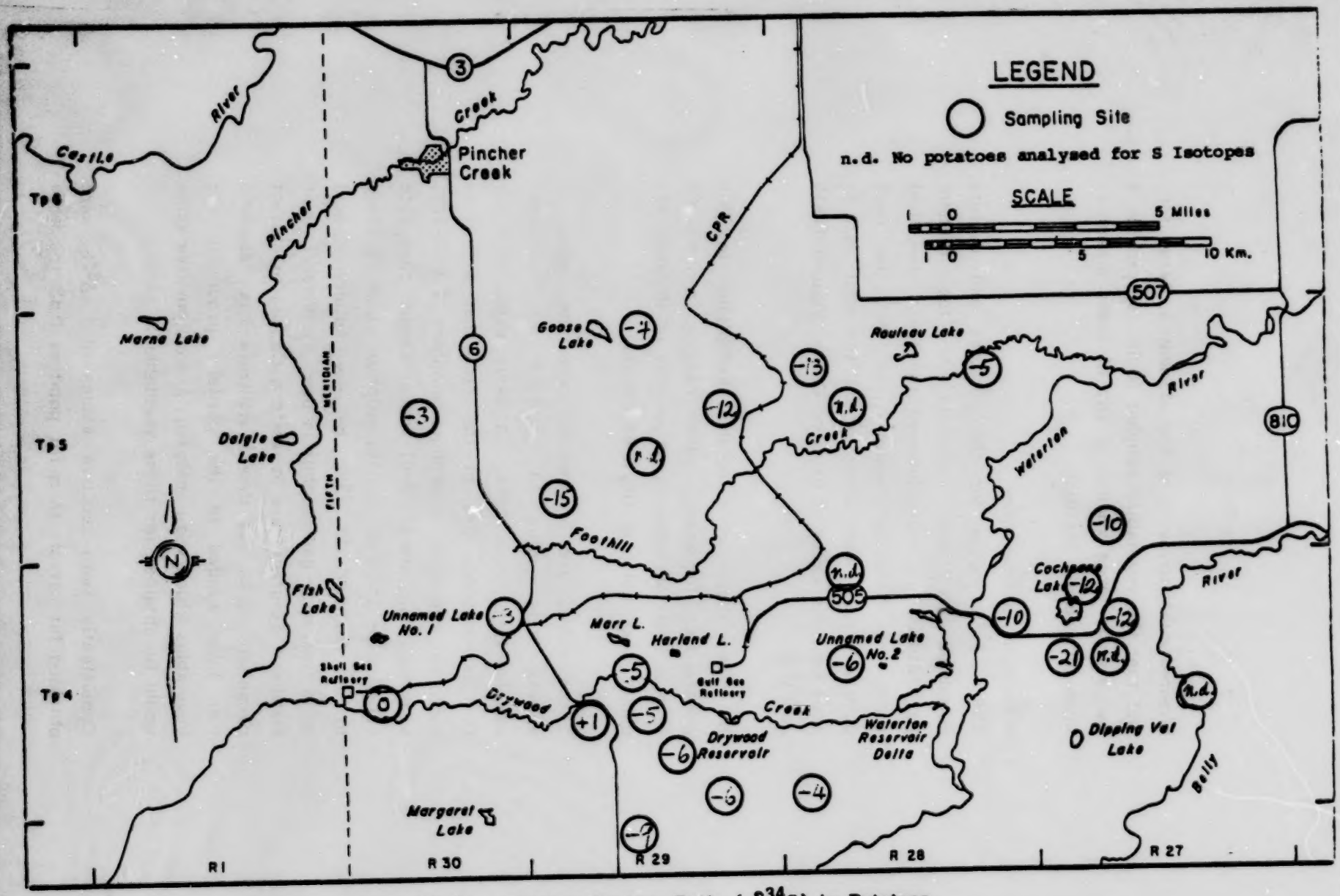


Figure IV-15. Sulphur Isotope Ratio ($\delta^{34}S$) in Potatoes.

Source: Krouse, University of Calgary, 1984, TASK FORCE.

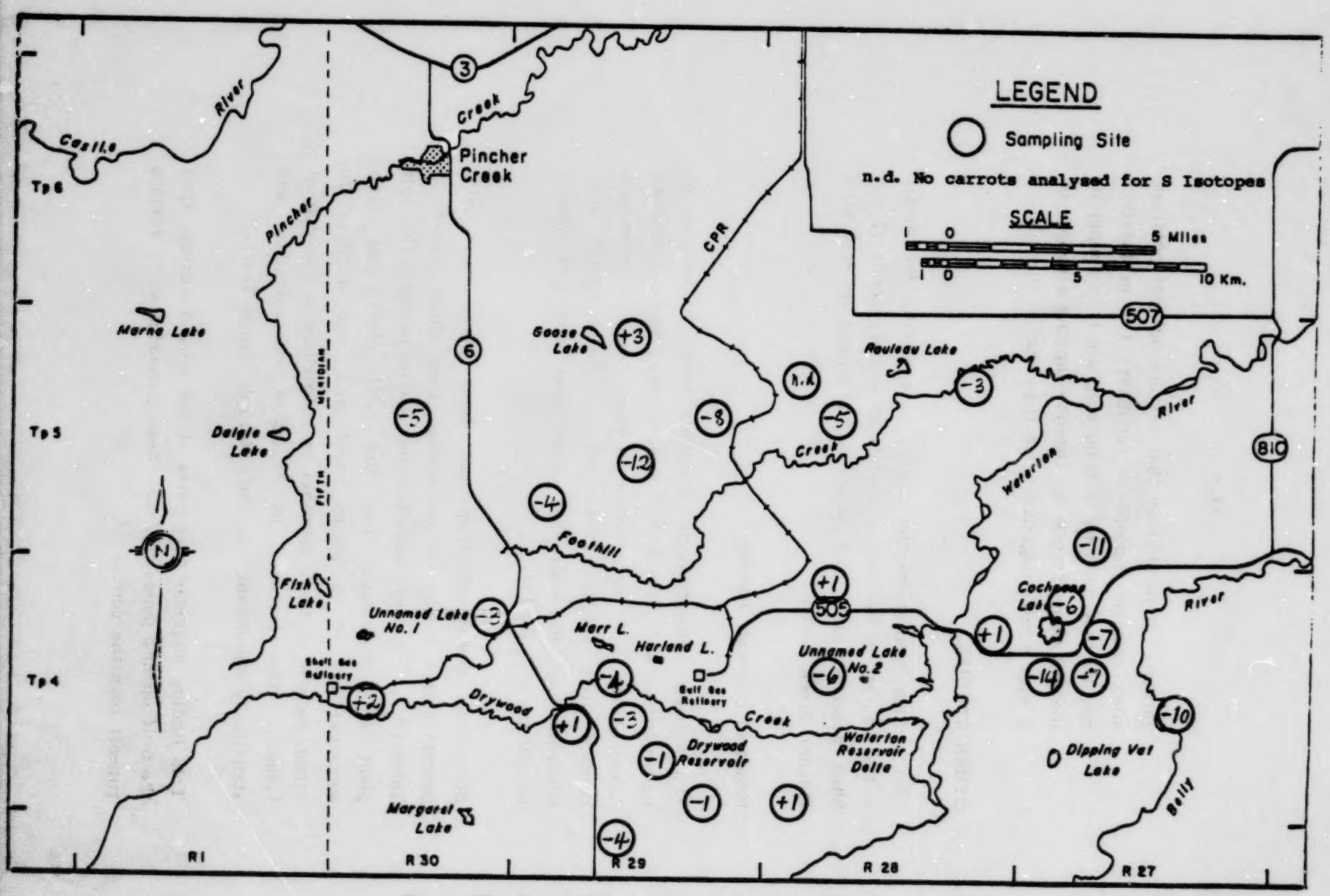


Figure IV-16. Sulphur Isotope Ratio in Carrots.

Source: Krouse, University of Calgary, 1984, TASK FORCE.

garden. It is unlikely that carrots but not potatoes often received phosphate fertilizer; the explanation may be that potatoes take up sulphate from deeper in the soil than carrots do, thereby tapping a source of S with a more negative value than that in topsoil.

OTHER STUDIES

This section summarizes the results of analyzing for metals and S isotopes in bullrushes, metals in settling ponds at the Shell Waterton plant and selenium in topsoil at the Gulf Pincher Creek plant.

Metals in Bullrush Samples

The highest concentrations of metals found in samples of bullrush tops and roots from Goose, Dipping Vat and Rouleau Lakes (Table IV-4) were similar to those found in grass and surface litter (Figure IV-4) and can be compared with concentrations in bullrushes from near the gas plants (Appendix S-1, p. 12).

Bullrushes downslope from the Shell plant had metal concentrations similar to or smaller than those shown in Table IV-4. However, some bullrushes from ponds at the Gulf plant and downslope from the Gulf plant had high concentrations of chromium, lead and zinc relative to concentrations of these elements in bullrushes at the distant lakes. The increase in chromium concentration was statistically significant (Duncan's Multiple Range Test).

This finding suggests that parts of the area downslope from the Gulf settling ponds may have been contaminated by surface run-off from the ponds.

Table IV-4

Highest Concentration (ppm) of Various Metals Found in Bullrush Tops and Roots From Three Lakes Approximately 15 km From the Shell and Gulf Gas Plants

Metal	Tops	Roots
As	0.54	3.3
Be	0.05	1.4
Cd	0.11	1.3
Cr	2.3	7.4
Cu	2.8	11
Hg	0.07	0.11
Ni	0.46	5.2
Pb	2.5	0.1
Se	0.04	0.14
Zn	13	36

Source: Saskatchewan Research Council, 1983, TASK FORCE.

Sulphur Isotopes in Bullrush Samples

The results of analyzing bullrush tops and roots for ^{34}S: ^{32}S ratios are summarized in Figure IV-17. The results for the Gulf pond and Goose Lake bullrushes lie on the line where $\delta^{34}S$ for roots equals that for tops, whereas other examples gave results in which $\delta^{34}S$ for tops was much more positive than that for roots. These results are capable of various interpretations, and further discussion would not be useful for present purposes.

Metals in Settling Ponds at the Shell Plant

The results of analyzing nine of the settling ponds at the Shell plant (Appendix S-1) show that sediment samples from those ponds contained concentrations of metals higher than those found in lake sediments by a factor of approximately 2 generally and, in some instances, by a factor of approximately 5.

This finding is not surprising given the function of the settling ponds. Concentrations of cadmium, mercury and zinc were similar to those reported by Monenco Ltd. in their preliminary estimate of pond sludge residues at the Gulf plant (Table IV-5). Concentrations of chromium were much less in the Shell plant sediment than at the Gulf plant, due presumably to the absence of chromium compounds from the Shell processing treatment.

The volumes of sludge in these ponds are difficult to estimate but an attempt has been made, assuming that the surface area of the sludge is equal to three quarters of the

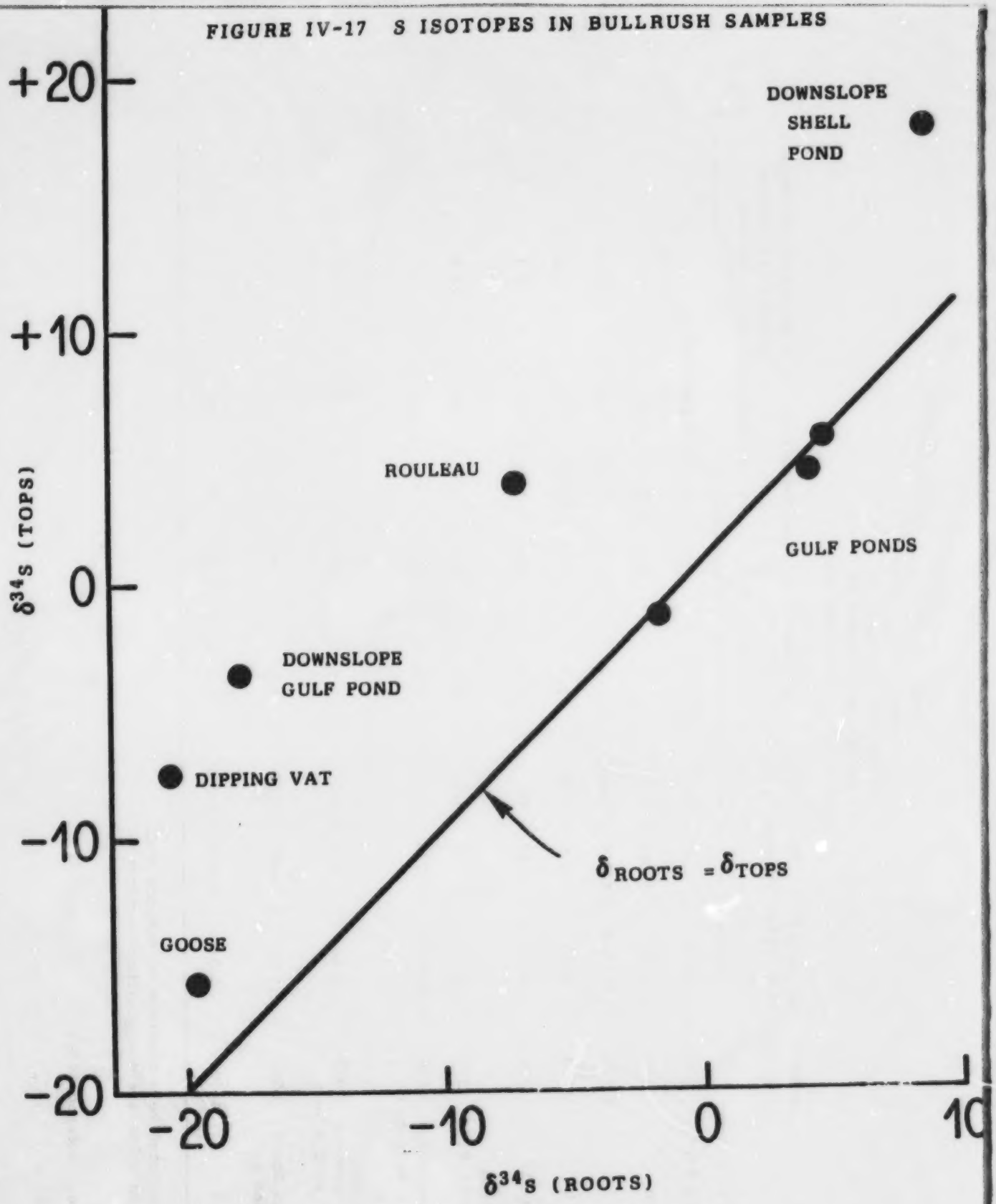
Table IV-5
Preliminary Estimate of
Pond Sludge Volumes* at
Gulf Pincher Creek Gas Plant

Pond	Area m^2	Estimated Sludge Depth m	Estimated Sludge Volume m^3	Estimated Average Composition of Significant Parameters Cd mg/kg	Cr mg/kg	Hg mg/kg	Zn mg/kg	Hydrocarbon Content (% in dry sed.)
Pond 6 Weir	100	0.70	45 - 70	3.1	795	0.73	215	0.4
Pond 6	7100	0.30	1560 - 2130	1.9	310	0.27	125	1.3
Pond 7	14970	0.90/1.30	12140 - 16460	7.2	1860	0.14	335	0.57
Pond 9	8590	0.60	3770 - 5150	3.0	710	0.88	175	0.4
Flare Pit	100	0.80	60 - 80	3.2	660	0.45	250	4.1
Existing Landfill Pit	370	1.15	320 - 325	6.9	760	1.9	360	11.4
Drainageway - Pond 6 Weir to Pond 6	2590	0.80/0.30	710 - 950	3.4	475	-	140	-
Drainageway - SW of Pond 6 Weir	970	0.35	250 - 340	1.8	720	-	175	-
Slough North of Pond 8	6260	1.0	4460 - 6260	1.1	26	-	44	-
Pond 8	14590	1.0	10670 - 14590	1.3	38	-	40	-

* Reproduced here courtesy of Monenco Ltd.
These volumes are approximate estimates.

Source: Monenco, 1983.

FIGURE IV-17 S ISOTOPES IN BULLRUSH SAMPLES



Source: Krouse, University of Calgary, 1984, TASK FORCE.

pond area. Sludge depths were assumed to be equal to the depth of sediment collected (Table E3, Appendix S-1) or assumed to be 0.2 m for those ponds not sampled. The sludge volumes thus calculated (Table IV-8) are expected to be accurate within a factor of 3 or 4. Not much weight can be placed on these calculations but they suggest that sludge volumes at the Shell Waterton plant are less than half the sludge volumes at the Gulf Pincher Creek plant.

Concentrations of metals in the water of the settling ponds were generally very small (Table IV-7). Only one pond (the aerobic digestion pond) had water exceeding the Canadian Drinking Water limit for cadmium and only one pond (the plant #2 slurry pond) had water exceeding the limits for mercury and chromium. These two ponds and three other ponds had arsenic concentrations above the specified limit.

It has already been stated in the chapter on Surface Water and Groundwater Hydrology that there is no sign that groundwater has been contaminated with heavy metals by seepage from the Shell plant settling ponds.

Selenium in Surface Soil at the Gulf Plant Site

The results of analyzing soil from three places on the Gulf site (Table IV-8) show that soil whose pH had been severely depressed by contamination with oxidized sulphur had considerably more total selenium than uncontaminated soil.

In view of this result, it seems unlikely that soil acidification caused by oxidation of wind-blown elemental sulphur would depress selenium uptake by vegetation and thereby induce selenium deficiency in grazing animals.

Table IV-6
Preliminary Estimate of Sludge Volumes at the Shell Waterton Sour Gas Plant

Pond	Estimated Area of Pond Surround (to nearest 500 m^3)	Sludge Volume (to nearest $100m^3$)
A	3,500	500
B	3,500	700
C	3,000	1,000
D	1,000	200
E	6,000	900
F	4,000	600
G	4,000	200
H	1,000	200
K	5,000	800
2	9,000	1,000
3	500	-
4	500	-
5	5,000	1,100
6	2,000	300
Surface Runoff		
Basin 1	6,000	900
Basin 2	2,000	200
Plant #2	5,000	800
Sludge Storage	1,000	100
Plant #2 Slurry	1,000	100
Aerobic Digestion	1,000	100
Sewage Lagoon	3,000	500

- pond not now in use.

Source: TASK FORCE, 1984.

Table IV-7
Concentrations of Metals in Settling Pond Water at the Shell Waterton Plant

Metal	Highest Concentration Found	Next Highest Concentration	Acceptable Drinking Water Limit
Hg	2.2 ppb	0.11 ppb	1.0 ppb
Se	0.002 ppm	<0.001 ppm	0.01 ppm
As	1.3	0.2	0.05
Be	0.01	0.003	-
Cd	0.07	0.004	0.005
Cr	0.22	0.05	0.05
Cu	0.23	0.20	1.0
Ni	0.12	0.11	-
Pb	0.014	0.010	0.05
Zn	1.4	0.82	5.0

- limit not given in "Guidelines for Canadian Drinking Water Quality" Supporting Documentation (1978).

Source: Saskatchewan Research Council, 1983, TASK FORCE.

Table IV-8
Selenium in Surface Soils From the Gulf Plant Site

Soil Location	pH	Selenium Content (ppm)
West of Process Area	7.4	<0.2
East of Sulphur Block	7.4	<0.2
Sulphur Block Run-off Area	3.2	1.1

Source: Saskatchewan Research Council, 1983, TASK FORCE.

CHAPTER FIVE

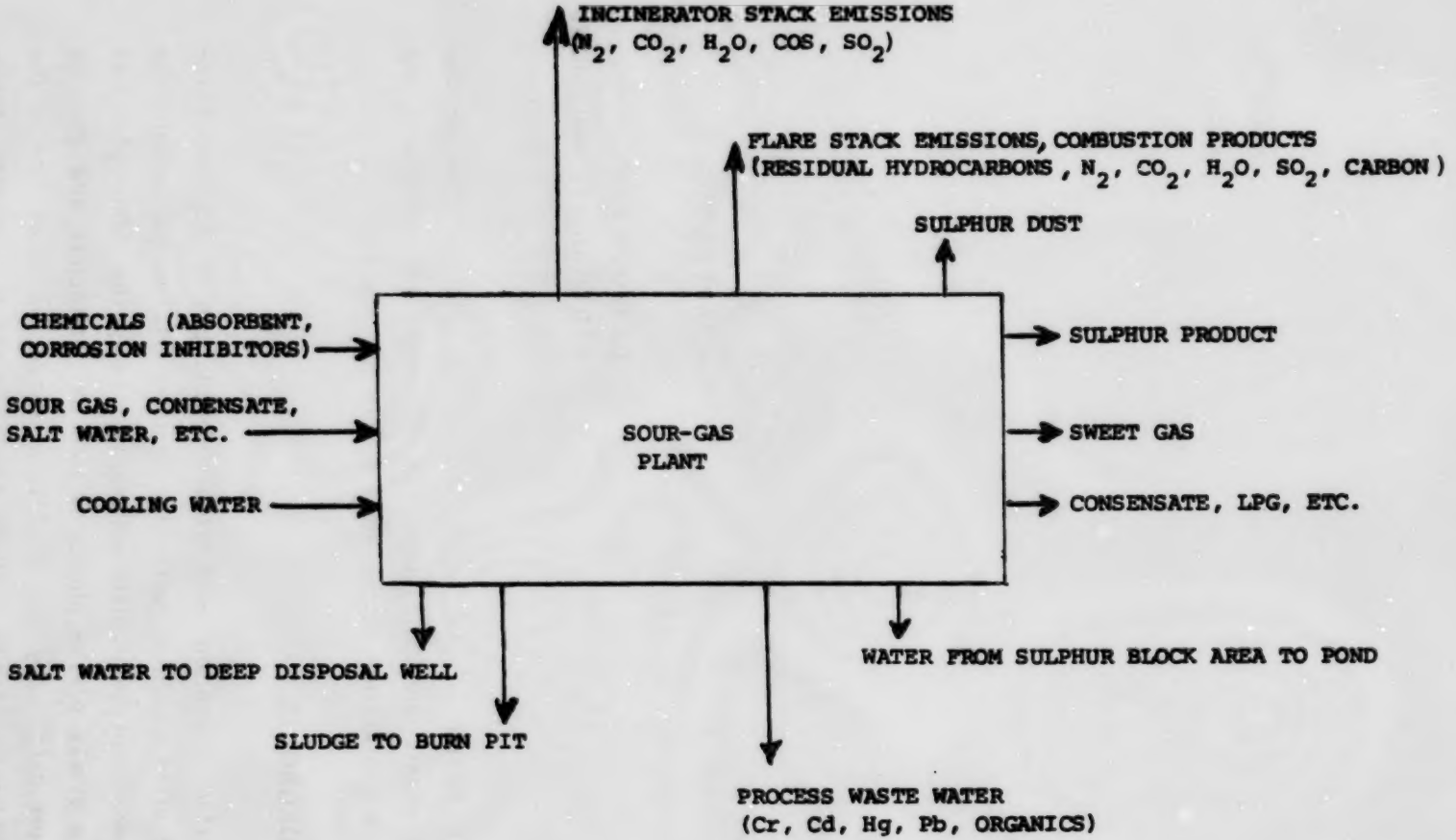
GASEOUS AND PARTICULATE EMISSIONS

This section of the report relates to the operation of the gas plants and considers the dispersal of substances by surface migration at the sites of the two plants.

BACKGROUND

"Surface migration" was discussed at length by the Task Force and after checking with the Minister, taken to include the gaseous and particulate emissions leaving the incinerator and flare stacks of the plants as well as particulate and gaseous matter carried by the wind from above the plant site to the neighbouring lands. These emissions are indicated in Figure V-1 showing a block diagram of the inputs and outputs from the plant.

Figure V-1 Block Diagram of Processing Operations


INCINERATOR STACK EMISSIONS
(N_2, CO_2, H_2O, COS, SO_2)
FLARE STACK EMISSIONS, COMBUSTION PRODUCTS
(RESIDUAL HYDROCARBONS, N_2, CO_2, H_2O, SO_2, CARBON)
SULPHUR DUST
CHEMICALS (ABSORBENT, CORROSION INHIBITORS)
SOUR GAS, CONDENSATE, SALT WATER, ETC.
COOLING WATER
SOUR-GAS PLANT
SULPHUR PRODUCT
SWEET GAS
CONSENSATE, LPG, ETC.
SALT WATER TO DEEP DISPOSAL WELL
SLUDGE TO BURN PIT
PROCESS WASTE WATER
(Cr, Cd, Hg, Pb, ORGANICS)
WATER FROM SULPHUR BLOCK AREA TO POND

Source: TASK FORCE, 1984.

REVIEW OF OTHER STUDIES

In view of this interpretation of the scope of the work to be undertaken, the results of several other studies were taken into consideration. A list of the reports dealing with other studies pertinent to this phase of the work is given along with the references at the end of this report.

Other reports relating to cleaning up the plant site have been considered and are also listed in the references.

Many questions have arisen as a result of examination and discussion of reports previously written. Much of the analytical work undertaken by the Task Force was done in an effort to provide answers to these questions so as to gain a better understanding of the processes involved with respect to the migration of substances in the subsurface, on the surface and in the air mass above the surface.

A brief review of some of these reports is undertaken hereafter to indicate some of the concerns of the Task Force which in many instances led to further investigations in attempts to provide answers.

Trace Element Emissions From the Incinerator Stacks (1)

This study was undertaken by the University of Windsor to determine the nature and the amounts of elements being released from the incinerator stacks from the Gulf Pincher Creek and Shell Waterton plants. The average emission rates

of aluminum, copper, iron, titanium and zinc from the Gulf plant were found to be 8.1, 1.7, 3.8, 8.0, and 1.3 g/h while from the Shell plant they were 69, 8.0, 71, 140 and 22 g/h respectively. While the Windsor group did show in another publication (2), that the inhaled quantities of the elements would be negligible compared with amounts ingested in food by people in the affected area, questions were, nevertheless, raised. What were the possible sources of these elements? Did the relatively small rates of emission represent the total output from the plant or could there be additional amounts, for example, in produced condensate and sour water? If so, were they likely to have any effect on the soil, animals and people in the area?

Trace Organics in the Downwind Atmosphere

In this study, by Strosher of the Kananaskis Centre (3), samples of the ambient air were taken in the vicinities of the Gulf Pincher Creek and Shell Waterton plants in the fall of 1981. In each case, trace quantities of many hydrocarbons were detected. These hydrocarbons, for the most part, are typical of compounds which might be expected to occur in condensate. Others were not typical of condensate. Questions therefore arose as to the sources of these compounds and whether in the small concentrations detected they could constitute a health hazard.

The Sciex Air Quality Survey (4)

Using a mobile, positive ion mass spectrometer, Sciex was able to detect qualitatively many fragments of organic and

inorganic molecules downwind from the Gulf and Shell plants. Again questions arose as to the sources of the organic and inorganic compounds responsible for these fragments. Many of these compounds do not appear in condensate as produced.

The Scientific Methodology Assessment Committee Report (5)

A team of five scientists assessed the Strosher and Sciex reports in terms of the methodology employed and the results obtained. On the basis of certain compounds determined quantitatively as being present in the atmosphere downwind from the plants and the threshold limit values (occupational exposure limits) for those compounds, it was concluded that "adverse health effects would not be expected at such low levels".

The Snider Report (6)

Under the heading, "How Twin Butte Is Different", this report lists nine health items in which participants in the survey were different in terms of health. Whether any of these complaints could be related to components in the air downwind from the plant might be questioned. The need to know more about the composition of the air in the area was suggested.

This report indicates further that nearly one half of the Twin Butte residents report allergy problems. Again it is conceivable that such problems could arise from exposure to foreign components in the air suggesting the need for more knowledge regarding the composition of the air in the region.

Hair analysis done on samples taken from people in the Twin Butte and control area suggested that the hair of certain people was significantly lower with respect to calcium and magnesium and higher with respect to phosphorus than those in the control areas. Also, their hair was statistically lower in selenium and higher in iron. These analyses "also revealed bio-clinical differences when grouped scores for elements were considered instead of absolute scores. Respondents from Twin Butte were proved to have significantly higher levels for two essential minerals, chromium and iron, and two toxic metals, mercury and cadmium, when compared with both control sites". It was stated further that "Downwind status from the two gas plants was determined to be the most statistically significant predictor of health symptom factor scale scores ...." and that "downwind status is also statistically associated with higher levels of family cancer and a number of allergies".

The terms of reference under which the Task Force operated do not include a study of health effects. However, in view of the above comments from the Snider Report, it became apparent that in analyzing the air, dust, water and soil in the area, special emphasis should be given to those elements and compounds which may in any known way contribute to the possible problems as outlined in the Snider Report.

Air Quality Surveys

The results of two ambient air quality surveys done by Alberta Environment over the period March 1 to May 31, 1980 and January 1 to March 24, 1982 (7,8) showed that only

hydrogen sulphide and ozone exceeded air quality standards for short periods. The other six pollutants monitored during the surveys - sulphur dioxide, total oxides of nitrogen, nitrogen dioxide, total hydrocarbons, carbon monoxide and soiling index, met the air quality standards. While the hydrogen sulphide and ozone exceeded the standards for short periods, the values recorded were well below levels at which health effects had been documented. It was interesting to note from the report for the period January - March 1981 that when the wind blew, 32% of the time it was from the west and that its average wind speed was 13.2 km/h. When blowing from other directions its speed was 7.6 km/h or less. Average wind speed was 6.1 km/h and 41.4% of the time the weather was calm. For this particular period one would therefore expect a large portion of the gaseous pollutants and the particulates from the two plants to be swept in an easterly direction.

"Effects on Crops and Livestock"

The study of the "Effects of Airborne Emissions from a Gas Processing Plant on Crops and Livestock"(9) by McKinnon, Allen and Associates gives the results of a five-year study. The effects of the plant emissions on crop yields, soil pH, sulphur budgets, sulphate and pH in rainfall as well as on swine, chickens, mice and cattle are given. From this study the need to determine the extent to which sulphur has been deposited over the area from the plant emissions has arisen. To what extent has acid rain in the area affected soil pH? How much of the buffering capacity of the soil in the area has been consumed? Is the soil likely to suffer a dramatic

decrease in pH if plant operations continue until the gas fields are depleted?

Site Clean-up and Reclamation

The report, "The Pincher Creek Gas Plant Site Clean-up and Reclamation, Report 2: An Initial Study", by Monenco Consultants Ltd (10), deals with on-site pollution of the soil and water. It does not include analyses of the effluents from the incinerator or flare stack. However, many of the hydrocarbons which have been detected in the soil and pond sediments are probably of the same origin i.e. the condensate, as the hydrocarbons detected in the air downwind from the plant. This correspondence will be considered.

"Pincher Creek Site Reclamation
- Twin Butte Public Meeting,
Questions and Answers"

This report prepared by Gulf Canada Resources Inc. for the meeting on March 21, 1983 was considered in terms of the questions it raises (11).

Selenium Levels

Two evaluations of the selenium levels in the Pincher Creek - Waterton area were undertaken by M. T. Strosher of the Kananaskis Centre for Environmental Research (12,13). The results obtained based on the selenium contents of the air and water determined and estimates of human dietary intake in Canada, indicate that selenium intakes for this area actually fall below the recommended intake to prevent selenium

deficiency along with related health problems. In view of this conclusion, the need to emphasize analyses for selenium in the soil, water and vegetable matter in the area was indicated to determine whether the values obtained fall within what might be considered a "normal range".

Discussions With Concerned Citizens

From discussions with concerned citizens who requested meetings with the Task Force, it became evident that air quality downwind from the gas plants has been a major cause of complaints. Due to the nature of the terrain and the variable flow patterns of the winds, it is thought that, at times, emissions from the stacks tend to accumulate in the valleys creating problems for the residents. With a shift in the winds, these contaminated air masses may be blown over other areas causing the people in these areas to be subjected to any pollutants which may be present. Personnel from the Shell Waterton Plant indicated that carbonyl sulphide had been detected in the incinerator stack effluent and this has been written up in the Shell Waterton News, November 1, 1983 as being the cause of the odor associated with stack emissions. Carbonyl sulphide is one of several odoriferous, sulphur-containing compounds which might be anticipated to be present in emissions from flare stacks.

Along with the above mentioned sulphur-containing compounds, there are many other organic compounds which could possibly be produced by incomplete combustion of waste gas in the flare stacks. Some of these might also be responsible for unpleasant odors in the atmosphere downwind from the plants. The need to analyze gases being emitted from the flare stacks during flaring operations was evident as was the need to

analyze the ambient air downwind from the plants. Analyses not only for organic components, but also for both organic and inorganic components containing sulphur, most of which have strong odors, were considered necessary.

TASK FORCE RESEARCH

The program undertaken to determine the nature, sources and distribution of components leaving the Gulf and Shell plants via the air mass is outlined below.

Metal Components Dispersed via the Incinerator Stacks

In their survey of the incinerator stacks at the Gulf and Shell plants, the University of Windsor team found aluminum, copper, iron, titanium and zinc being emitted in quantities ranging from approximately 1.0 to 140 g/h. It may be speculated that the aluminum could have come from the alumina catalyst used in the Claus process, the titanium from firebrick in the furnaces, the iron from the steel equipment in the plant and the zinc possibly from a heat exchanger. No satisfactory explanation based on materials used in the plant could be obtained to explain the presence of copper in the stream. In view of this problem, it was decided to analyze samples of the soil and dust in the air taken near the blowers which provide(d) air to the Claus burner at each plant site. It was argued that any dust picked up could be fed through the reaction system to the incinerator stack and might provide a reasonable source for the elements which were detected.

Filters for a "Hi Vol" sampler similar to those used in previous work on the incinerator stacks were obtained from Dr. Carl St. Pierre at the University of Windsor. Samples of dust were collected on "Hi Vol" samplers by Strosher and Parker of the Kananaskis Centre at the above-mentioned locations. The samples together with blanks were submitted to Dr. St. Pierre who used the same methods applied in the analysis of the incinerator effluent stream as were used for the various elements on which that group reported results to the Energy Resources Conservation Board (1). The analyses of the dust samples are reported in Table V-1.

Some 12 soil samples were taken in the vicinity of each air supply blower for the Claus unit at the two plants and an additional 12 samples were taken as a control from an area west of the Shell plant. These samples were composited and a representative sample of each composite was sent to Dr. W. Yuen at the Saskatchewan Research Council for analysis. Dr. Yuen was instructed to use ICP analysis for aluminum (Al), copper (Cu), iron (Fe), titanium (Ti), zinc (Zn), cadmium (Cd), tin (Sn) and chromium (Cr); hydride generation for selenium (Se), arsenic (As), and antimony (Sb); atomic absorption for lithium (Li) and tin (Sn) and finally the cold vapor method for mercury (Hg) analysis. The results of these analyses appear in Table V-2.

Selenium Levels in the Soil on the Plant Site

Since the chemistries of selenium and sulfur are similar, one might wonder whether the soil on the Gulf plant site might have been contaminated with selenium associated with the

Table V-1 Summary of Trace Element Analyses for Hi-Vol Filters at Hydrogen Sulphide Combustion Furnaces at the Gulf and Shell Plants.

Filter Element	Shell Plant No. 1057136	Gulf Plant No. 1057137	Blank No. 1057138	Blank No. 1057139
		Total Mass in Micrograms		
Total Particulate	42,100	134,000	--	--
Ag Silver	< 6	< 6	< 6	< 6
Al Aluminum	800	900	< 500	< 500
As Arsenic	2	4	< 1	2
B Boron	< 1000	< 1000	< 1000	< 1000
Be Beryllium	< 1	< 1	< 1	< 1
Cd Cadmium	4	2	< 2	< 2
Co Cobalt	< 10	< 10	< 10	< 10
Cr Chromium	< 20	< 20	< 20	< 20
Cu Copper	980	420	< 10	< 10
Fe Iron	380	2000	< 10	< 10
Ga Gallium	< 200	< 200	< 200	< 200
Ge Germanium	< 100	< 100	< 100	< 100
Hg Mercury	< 6	< 6	< 6	< 6
In Indium	< 100	< 100	< 100	< 100
Li Lithium	< 3	3	< 3	< 3
Mn Manganese	10	58	< 6	< 6
Mo Molybdenum	< 20	< 20	< 20	< 20
Ni Nickel	< 20	< 20	< 20	< 20
Pb Lead	20	80	< 20	< 20
Sb Antimony	< 20	< 20	< 20	< 20
Sc Scandium	< 30	< 30	< 30	< 30
Se Selenium	< 2	< 2	< 2	< 2
Sn Tin	< 50	< 50	< 50	< 50
Sr Strontium	< 6	9	< 5	< 5
Te Tellurium	< 60	< 60	< 60	< 60
Ti Titanium	< 60	< 60	< 60	< 60
Tl Thallium	< 60	< 60	< 60	< 60
V Vanadium	< 60	< 60	< 60	< 60
Zn Zinc	65	45	< 2	< 2

Table 1: Summary of Trace Element Analyses for Hi-Vol Filters Employed In the Areas of the Hydrogen Sulfide Combustion Furnaces at the Gulf and Shell Plants

Source: University of Windsor, TASK FORCE, 1984.

Table V-2 Analysis of Trace Metals and Trace Constituents in Soil

SRC Group: 1437 01-Dec-83 11:54 AM Page 1

SASKATCHEWAN RESEARCH COUNCIL

University of Calgary
Dept. Chemical & Petroleum Eng.
2500 University Drive N.W.
Calgary, Alberta T2N 1N4
Attn: Eric Tollefson

Date Samples Received: 09-Nov-83 Client P.O.:

SAMPLE CLIENT DESCRIPTION
9521 SOIL @ CLAUS AIR INTAKE GULF PLANT *SOIL*
9522 SHELL GAS PLANT SOIL @ CLAUS BLOWER *SOIL*
9523 SOIL W OF SHELL PLANT *SOIL*

ANALYTE	UNITS	9521	9522	9523
TRACE CONSTITUENTS				
Hg, solids	ug/g	3.5	0.06	<0.03
Se, solids	ug/g	<0.5	<0.5	<0.5
TRACE METALS				
Al, ICP-AES	ug/g	23000	32000	46000
As, solids	ug/g	8.9	13	11
Cd, ICP-AES	ug/g	0.7	<0.5	<0.5
Cr, ICP-AES	ug/g	60	95	50
Cu, ICP-AES	ug/g	43	23	17
Fe, ICP-AES	ug/g	22000	28000	28000
Li, by A.A.	ug/g	14	28	44
Sb, hydride gen	ug/g	<0.5	<0.5	<0.5
Sn, by A.A.	ug/g	<100	<100	<100
Ti, ICP-AES	ug/g	920	340	370
Zn, ICP-AES	ug/g	340	120	80

Source: Saskatchewan Research Council, TASK FORCE, 1984.

sulphur from the sulphur block and the associated dust. For this reason Gulf was asked to provide three samples of soil to determine whether there was any substance to this possibility. Samples of soil were therefore taken west of the plant site (as a control), on the plant site on land above the sulphur block area and on the plant site in the drainage area below the sulphur block. These samples were sent to Dr. Yuen for analyses using methods he applied with other soil samples. The results appear in Table V-3.

Condensate and Pentanes-Plus as Heavy Metal Sources

It is known that some heavy metals can combine with certain organic molecules to form organometallic compounds. The question arose as to whether heavy metals might have been obtained from the gas-producing formations via these compounds. If this were possible and such material were carried to a flare during a plant upset, then the organometallic compound could be burned and fragments discharged to the atmosphere. It also seemed possible that such compounds might find their way after spills via the drainage system to the settling ponds. For these reasons, Strosher and Parker of the Kananaskis Centre were requested to obtain samples of condensate from the Gulf plant and from the streams recovered from Sheets 3 and 4 from the Shell Waterton field. In addition, two samples of another condensate fraction known as "pentanes-plus" from the Shell Waterton plant were requested. In both instances, through the cooperation of plant personnel, the samples requested were provided. These samples were delivered to Metro Tech Systems Ltd. in Calgary for analyses. In addition,

Table V-3 Analysis for Trace Constituents of Soil near Gulf Plant

SRC Group: 385 10-Apr-84 09:55 AM Page 1

SASKATCHEWAN RESEARCH COUNCIL

Norwest Labs
9938-67 Avenue
Edmonton, Alberta T6E oP5
Attn: Dr. John Ashworth

APR 10 '84

Date Samples Received: 25-Mar-84 Client P.O.:

SAMPLE	CLIENT DESCRIPTION
3170	PINCHER CR GAS PLANT (GULF) #33 0-6" *SOIL*
3171	PINCHER CR GAS PLANT (GULF) #10-2 0-15 CM *SOIL*
3172	SULFUR BLOCK RUNOFF AREA (DEN-DEN ENT.LTD) *SOIL*

ANALYTE	UNITS	3170	3171	3172
TRACE CONSTITUENTS				
Se, sep digest	ug/g	<0.2	<0.2	1.1
PHYSICAL PROPERTIES				
pH on solids	pH units	7.37	7.43	3.15

Source: Saskatchewan Research Council, TASK FORCE, 1984.

benzene-toluene "blank" samples were included to determine whether there might have been any significant amount of metals "picked up" from the steel sample bomb by these aromatic hydrocarbons. The analyses appear in Tables V-4 to V-9.

Analysis of Sour Water Samples

As a further check on possible sources of heavy metals, samples of the sour water produced with the gas from the Gulf Pincher Creek field and from the Sheet 3 and 4 formations of the field used by the Shell Waterton plant were requested. In each case samples were provided through the cooperation of plant personnel. The samples were analyzed by Metro Tech Systems Ltd. in Calgary, and the results are given in Tables V-10 through V-12.

Isotopic Sulfur Analyses as a Means of Tracing the Deposition of Sulfur

From papers by Dr. Roy Krouse at the University of Calgary, it is known that the S^{34}/S^{32} ratio in sulfur compounds produced with sour gas is different from this ratio measured on sulfur occurring naturally in the surface soils of the land surrounding these plants. This technique provides a powerful tool by which it is possible to determine the extent of deposition of sulfur at various points in the area surrounding the plants. For the above and other reasons, it was decided to determine the isotopic sulfur ratios of:

- the hydrogen sulfide in the sour gas,

Table V-4 Analysis of Condensate after Venting Light Ends - Gulf, Pincher Creek

Our Sample Number: 9201

Your Sample: Gulf, Pincher Creek, Condensate after venting light ends

Silver	<40 PPB	Aluminum	<100 PPB
Arsenic	<0.2 PPM	Boron	<0.01 PPM
Barium	<5 PPB	Beryllium	<5 PPB
Calcium	<2 PPB	Cadmium	<20 PPB
Chromium	<70 PPB	Copper	<10 PPB
Iron	<40 PPB	Mercury	0.10 PPM
Potassium	3.35 PPM	Magnesium	<1 PPB
Manganese	<1 PPB	Molybdenum	<0.02 PPM
Sodium	1.92 PPM	Nickel	0.95 PPM
Phosphorous	<0.1 PPM	Lead	<0.01 PPM
Selenium	<0.1 PPM	Silicon	0.60 PPM
Tin	<0.1 PPM	Titanium	<0.02 PPM
Vanadium	<10 PPB	Zinc	<0.01 PPM
Cobalt	<0.01 PPM	Lithium	<30 PPB
Thallium	<70 PPB	Germanium	<0.1 PPM
Gallium	<0.1 PPM	Scandium	<0.03 PPM
Antimony	<0.03 PPM	Strontium	<10 PPB
Indium	<1 PPM	Tellurium	<0.02 PPM

Remarks: Gases bled off, 100 cc's drained off and concentrated down to 10 cc's, over low heat and ambient pressure. Metals are on the 10 cc's portion.

Note trace presence of Indium.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-5 Analysis of Condensate after Venting Light Ends - Shell Waterton, Sheet 3

Our Sample Number: 9199

Your Sample: Shell, Waterton, Sheet 3, after Venting Light Ends

Silver	<40 PPB	Aluminum	<100 PPB
Arsenic	<0.2 PPM	Boron	<0.01 PPM
Barium	0.09 PPM	Beryllium	<5 PPB
Calcium	<2 PPB	Cadmium	<20 PPB
Chromium	<70 PPB	Copper	0.02 PPM
Iron	<40 PPB	Mercury	<0.01 PPM
Potassium	3.67 PPM	Magnesium	<1 PPB
Manganese	<1 PPB	Molybdenum	<0.02 PPM
Sodium	2.13 PPM	Nickel	0.80 PPM
Phosphorous	<0.01 PPM	Lead	<0.01 PPM
Selenium	2.77 PPM	Silicon	<0.02 PPM
Tin	<0.1 PPM	Titanium	<0.02 PPM
Vanadium	<10 PPB	Zinc	<0.01 PPM
Cobalt	<0.01 PPM	Lithium	<30 PPB
Thallium	<70 PPB	Germanium	<0.1 PPM
Gallium	<0.1 PPM	Scandium	<0.03 PPM
Antimony	<0.03 PPM	Strontium	<10 PPB
Indium	<1 PPM	Tellurium	<0.02 PPM

Remarks: Gases bled off, 100 cc's of liquid collected and concentrated under low heat and ambient pressure to 10 cc's. Metals above are on the 10 cc's portion.

Note also Indium in trace amounts.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-6 Analysis of Condensate after Venting Light Ends - Shell Waterton, Sheet 4

Our Sample Number: 9200

Your Sample: Shell, Waterton, Sheet 4, Condensate after venting Light Ends

Silver	< 40 PPB	Aluminum	< 100 PPB
Arsenic	< 0.2 PPM	Boron	< 0.01 PPM
Barium	< 5 PPB	Beryllium	< 5 PPB
Calcium	4.96 PPM	Cadmium	0.03 PPM
Chromium	< 70 PPB	Copper	0.05 PPM
Iron	3.86 PPM	Mercury	0.18 PPM
Potassium	3.12 PPM	Magnesium	0.30 PPM
Manganese	0.03 PPM	Molybdenum	< 0.02 PPM
Sodium	6.74 PPM	Nickel	0.81 PPM
Phosphorous	< 0.1 PPM	Lead	< 0.01 PPM
Selenium	13.75 PPM	Silicon	< 0.02 PPM
Tin	< 0.1 PPM	Titanium	< 0.02 PPM
Vanadium	< 10 PPB	Zinc	< 0.01 PPM
Cobalt	< 0.01 PPM	Lithium	< 30 PPB
Thallium	< 70 PPB	Germanium	< 0.1 PPM
Gallium	< 0.1 PPM	Selenium	< 0.03 PPM
Antimony	< 0.03 PPM	Strontium	< 10 PPB
Indium	< 1 PPM	Tellurium	< 0.02 PPM

Remarks: Gases bled off, 100 cc's liquid withdrawn and concentrated down to 10 cc's over low heat and ambient pressure. Metals above are on 10 cc's portion.

Note presence of Indium.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-7 Analysis of "Pentanes Plus" Shell Waterton, Sample 1

Our Sample Number: 9196

Your Sample: Pentanes plus, Shell Waterton, Sample 1

Silver	<40 PPB	Aluminum	<100 PPB
Arsenic	<0.2 PPM	Boron	0.2 PPM
Barium	0.08 PPM	Beryllium	< 5 PPB
Calcium	<2 PPB	Cadmium	<20 PPB
Chromium	<70 PPB	Copper	<10 PPB
Iron	<40 PPB	Mercury	<0.1 PPM
Potassium	3.60 PPM	Magnesium	<1 PPB
Manganese	<1 PPB	Molybdenum	<0.02 PPM
Sodium	2.21 PPM	Nickel	0.9 PPM
Phosphorous	1.80 PPM	Lead	<0.01 PPM
Selenium	1.30 PPM	Silicon	3.15 PPM
Tin	<0.1 PPM	Titanium	<0.02 PPM
Vanadium	<10 PPB	Zinc	1.75 PPM
Cobalt	<0.01 PPM	Lithium	< 30 PPB
Thallium	<70 PPM	Germanium	< 0.1 PPM
Gallium	<0.1 PPM	Scandium	<0.03 PPM
Antimony	<0.03 PPM	Strontium	< 10 PPB
Indium	<0.04 PPM	Tellurium	<0.02 PPM

Remarks: Gases were vented, then 300 cc's of liquid were poured out; this was concentrated under low heat and ambient pressure to 50 cc's. Metals above are on the 50 cc. concentrate.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-8 Analysis of "Pentanes Plus" Shell Waterton, Sample 2

Our Sample Number: 9197

Your Sample: Pentanes plus, Shell Waterton, Sample 2

Silver	< 40 PPB	Aluminum	<100 PPB
Arsenic	< 0.2 PPM	Boron	< 0.01 PPM
Barium	< 5 PPB	Beryllium	< 5 PPB
Calcium	< 2 PPB	Cadmium	< 20 PPB
Chromium	< 70 PPB	Copper	< 10 PPB
Iron	0.90 PPM	Mercury	< 0.1 PPM
Potassium	2.90 PPM	Magnesium	< 1 PPB
Manganese	< 1 PPB	Molybdenum	< 0.02 PPM
Sodium	1.86 PPM	Nickel	0.69 PPM
Phosphorous	2.10 PPM	Lead	< 0.01 PPM
Selenium	8.08 PPM	Silicon	3.16 PPM
Tin	< 0.01 PPM	Titanium	< 0.02 PPM
Vanadium	< 10 PPB	Zinc	2.04 PPM
Cobalt	< 0.01 PPM	Lithium	< 30 PPB
Thallium	< 70 PPB	Germanium	< 0.1 PPM
Gallium	< 0.01 PPM	Scandium	< 0.03 PPM
Antimony	< 0.03 PPM	Strontium	< 10 PPB
Indium	< 1 PPM	Tellurium	< 0.02 PPM

Remarks: Gases were vented, then 300 cc's of liquid were poured out; this was concentrated under low heat and ambient pressure to 50 cc's. Metals above, are on the 50 cc's concentrate.

Note Indium, our standard detection limit is 0.04 ppm, hence we obtained a trace in this sample.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-9 Analysis of Benzene - Toluene Blank

Our Sample Number: 9198

Your Sample: Benzene - Toluene Blank

Silver	<40 PPB	Aluminum	<100 PPB
Arsenic	<0.2 PPM	Boron	<0.01 PPM
Barium	<5 PPB	Beryllium	<5 PPB
Calcium	<2 PPB	Cadmium	<20 PPB
Chromium	<70 PPB	Copper	<10 PPB
Iron	<40 PPB	Mercury	<0.1 PPM
Potassium	6.85 PPM	Magnesium	<1 PPB
Manganese	<1 PPB	Molybdenum	<0.02 PPM
Sodium	3.16 PPM	Nickel	1.52 PPM
Phosphorous	<0.1 PPM	Lead	<0.01 PPM
Selenium	<0.1 PPM	Silicon	<0.02 PPM
Tin	<0.1 PPM	Titanium	<0.02 PPM
Vanadium	<10 PPB	Zinc	<0.01 PPM
Cobalt	<0.01 PPM	Lithium	<30 PPB
Thallium	<70 PPB	Germanium	<0.01 PPM
Gallium	<0.1 PPM	Scandium	<0.03 PPM
Antimony	<0.03 PPM	Strontium	<10 PPB
Indium	<0.04 PPM	Tellurium	<0.02 PPM

Remarks: 42 cc's drained off and concentrated to 10 cc's and then analysed.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-10 Analysis of Sour Water, Gulf Pincher Creek Plant

Our Sample Number 9195

Your Sample: Sour Water, Gulf, Pincher Creek

Silver	< 4 PPB	Aluminum	0.14 PPM
Arsenic	Note 1	Boron	55.18 PPM
Barium	0.45 PPM	Calcium	272.2 PPM
Cadmium	0.13 PPM	Chromium	0.11 PPM
Cobalt	0.16 PPM	Copper	0.02 PPM
Iron	0.43 PPM	Mercury	0.6 PPB
Potassium	441.8 PPM	Magnesium	55.60 PPM
Manganese	0.10 PPM	Molybdenum	0.01 PPM
Sodium	0.32 %	Nickel	0.04 PPM
Phosphorous	6.87 PPM	Lead	0.15 PPM
Selenium	< 20 PPB	Silicon	10.56 PPM
Tin	0.36 PPM	Titanium	5.76 PPM
Vanadium	< 2 PPB	Zinc	0.38 PPM
Beryllium	< 1 PPB	Antimony	1.27 PPM
Tellurium	< 20 PPB	Strontium	88.27 PPM
Lithium	28.12 PPM	Indium	< 40 PPB
Thallium	< 75 PPB	Scandium	< 1 PPB
Gallium	< 40 PPB	Germanium	< 100 PPB

Note 1: The actual test result for Arsenic was 6 PPM, however, due to some organic material perceived in the sample, I strongly suspect that this result is ficticious. I would recommend that this sample be tested for Arsenic by Atomic Absorption, using the Arsine Generation method.

Note 2: Hydrogen Sulfide was allowed to vent off, prior to testing.

Arsenic	< 10 PPB	} Check by A.A.
Cadmium	0.17 PPM	

Source: Metro Tech Systems Ltd., TASK FORCE, 1984.

Table V-11 Analysis of Sour Water, Shell Waterton Plant, Sheet 3

Our Sample Number: 9193

Your Sample: Shell Waterton Sour Water, Sheet 3

Silver	<4 PPB	Aluminum	<15 PPB
Arsenic	<25 PPB	Boron	0.89 PPM
Barium	<1 PPB	Calcium	18.89 PPM
Cadmium	<1 PPB	Chromium	0.008 PPM
Cobalt	0.04 PPM	Copper	<2 PPB
Iron	0.22 PPM	Mercury	11.2 PPB
Potassium	13.66 PPM	Magnesium	3.64 PPM
Manganese	0.07 PPM	Molybdenum	<5 PPB
Sodium	146.0 PPM	Nickel	0.01 PPM
Phosphorous	0.57 PPM	Lead	0.03 PPM
Selenium	<20 PPB	Silicon	<10 PPB
Tin	<6 PPB	Titanium	0.12 PPM
Vanadium	<2 PPB	Zinc	0.02 PPM
Beryllium	<1 PPB	Antimony	<30 PPB
Tellurium	<20 PPB	Strontium	0.31 PPM
Lithium	0.84 PPM	Indium	<40 PPB
Thallium	<75 PPB	Scandium	<1 PPB
Gallium	<40 PPB	Germanium	<100 PPB

Remarks: 1) Hydrogen Sulfide allowed to vent off before testing.

Source: Metro Tech Systems Ltd., TASK FORCE, 1984

Table V-12 Analysis of Sour Water, Shell Waterton Plant, Sheet 4

Our Sample Number: 9194

Your Sample: Shell, Waterton, Sour Water, Sheet 4

Silver	<4 PPB	Aluminum	<15 PPB
Arsenic	Note 1	Boron	121.2 PPM
Barium	<1 PPB	Calcium	451.9 PPM
Cadmium	0.60 PPM	Chromium	0.06 PPM
Cobalt	0.38 PPM	Copper	<2 PPB
Iron	0.28 PPM	Mercury	3.4 PPB
Potassium	718.6 PPM	Magnesium	73.87 PPM
Manganese	0.03 PPM	Molybdenum	0.04 PPM
Sodium	1.72 %	Nickel	0.06 PPM
Phosphorous	1.26 PPM	Lead	0.24 PPM
Selenium	<20 PPB	Silicon	0.04 PPM
Tin	1.30 PPM	Titanium	0.79 PPM
Vanadium	0.02 PPM	Zinc	1.22 PPM
Beryllium	<1 PPB	Antimony	2.31 PPM
Tellurium	<20 PPB	Strontium	13.63 PPM
Lithium	94.89 PPM	Indium	<40 PPB
Thallium	<75 PPB	Scandium	<1 PPB
Gallium	<40 PPB	Germanium	<100 PPB

Note 1: The actual test result for arsenic was 14 PPM, however, due to some organic material perceived in the sample, I strongly suspect the result is ficticious. I would recommend that this sample be tested for arsenic by Atomic Absorption Spectrometry, using the Arsine Generation method.

Note 2: Hydrogen Sulfide was allowed to vent off prior to testing.

Arsenic	<10 PPB	} Check by A.A.
Cadmium	0.95 PPM	

Source: Metro Tech Systems Ltd., TASK FORCE, 1984

- the sulfur dioxide emitted from the incinerator stack and
- the solid sulphur product from each plant.

To undertake this work, Dr. Krouse was asked to provide KOH/EDTA filters which can be fitted into Hi Vol samplers so that sulphur dioxide in the air can be effectively trapped and the S^{34}/S^{32} ratio measured. In addition, Dr. Krouse provided cadmium acetate traps which could be used to collect sulfur from the hydrogen sulfide present in the gas being produced at the Gulf site and from Sheets 3 and 4 of the gas producing formations at the Shell site. Again with the cooperation of personnel at both sites, Strosher and Parker of the Kananaskis Centre were able to obtain these samples and to pass them on to Dr. Krouse to determine the S^{34}/S^{32} ratios. The results of these analyses are considered in Chapter IV of the report. Through the courtesy of Mr. Lin Callow at Gulf and Mr. Ken Dickey of Shell, samples of the sulphur product from each plant were obtained to enable Dr. Krouse to do sulfur isotope ratios. The results of these analyses also are included in the same chapter.

Consideration of Pollution from Flare Stacks

A complete study of the gases leaving the flare stacks during flaring of various streams from the Shell Waterton plant would be a very expensive task in view of the difficulties seen in (a) obtaining representative samples, (b) the complexity of the analysis of samples containing perhaps hundreds of components and (c) the wide range of possible conditions and materials which might from time to time be

flared. The possibility of using a helicopter to assist with sample taking was discussed but dismissed because of the problems in getting truly representative samples, the cost and hazards involved. Other methods which would give an indication of the components present in the flare stack effluent were therefore considered for use although it was realized that the results would represent a very short term look at the picture as a whole.

In support of the above approach, it was decided to do downwind monitoring of the air and to take a few samples in the manner which Strosher of the Kananaskis Centre had used in his survey of "Trace Organic Compounds in the Atmosphere Near Industrial Development" (3). In addition, it was considered worthwhile to use a relatively new instrument of high sensitivity in the analysis of sulphur-containing compounds. This instrument (a Tracor Model 270HA Sulphur Gas Analyzer) is essentially a mobile gas chromatograph equipped with a flame photometer detector capable of detecting sulphur-containing compounds such as hydrogen sulphide, carbonyl sulphide, carbon disulphide, sulphur dioxide and some light mercaptans.

It was considered that in an initial survey of the flare stack emissions and as another check on the possible impurities in the ambient air, this combination of instruments would, within the financial restrictions of the Task Force, provide a reasonable scan of the components in the flare stack and downwind ambient air. The methodology and results of this work are provided in more detail in Appendix A-1 which is the report of M. T. Strosher entitled

"Twin Butte Source and Ambient Air Evaluation Study" to the Task Force.

RESULTS AND DISCUSSION

The results of the analytical studies undertaken are outlined below.

Analyses of Dust Samples

The analyses of dust samples taken in the vicinities of the Claus unit air blowers on the Gulf Pincher Creek and Shell Waterton plant sites are given in Table V-1. By comparison with two blank samples, it can be seen that the following elements were below the detectable limits of the analytical method: silver (Ag), boron (B), beryllium (Be), cobalt (Co), chromium (Cr), gallium (Ga), germanium (Ge), mercury (Hg), indium (In), molybdenum (Mo), nickel (Ni), antimony (Sb), scandium (Sc), selenium (Se), tin (Sn), tellurium (Te), titanium (Ti), thallium (Tl) and vanadium (V). Elements found present in significant proportions include: aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn), while those present in trace quantities were: arsenic (As), cadmium (Cd), lithium (Li) and strontium (Sr) (Li and Sr appearing in Gulf plant dust only).

It is of interest to note that in spite of the chromium pollution of the ponds on the Gulf plant site, no detectable quantity of chromium was found in the sample from that site. Also, no mercury was detected in the same sample even though there was some contamination of parts of the plant site with mercury. It is interesting to observe that selenium, if

present, was below the detectable limit of both dust samples. The fact that titanium was not detected in the dust is surprising. It was one of the components detected in significant levels in the incinerator stack gases by the University of Windsor group, and is normally found in high concentrations in soils.

The fact that aluminum, copper, iron and zinc were found in significant proportions supports the theory that the elements detected by the Windsor group may indeed have come from the dust in the air. In dust from the Gulf plant site, the quantity of copper present is about one fifth that of iron while in the dust from the Shell plant it is two to three times greater. In view of there being no other known source of copper, it would appear that the dust in the air was the source of the copper observed in the University of Windsor stack survey.

The fact that cadmium was found in trace quantities in the dust suggests that the dust in the area may be the source of the cadmium found in the Gulf Pincher Creek pond sediment samples. Tables 4.3, 4.4 and 4.5 of reference 10 give the compositions of samples taken from Pond 6, Pond 7 and Pond 9 areas, and show the presence of cadmium at concentrations ranging from about 1 to 5 ppm.

Analyses of Soil Samples

The analyses of soil samples taken near to the Claus air blower inlets at the Gulf and Shell plants and from a control area west of the Shell plant are given in Table V-2. In this instance, mercury (3.5 ppm) was found in the soil collected on the Gulf plant site supporting the contention that there

had been mercury spills in the operation of the plant and that the soil had been contaminated by this toxic element. The report by Monenco (13) deals with this matter in considerable detail.

The analyses of soil samples show the presence of very significant quantities of aluminum and iron (probably as their oxides). There are lesser quantities of titanium, zinc, copper, chromium, lithium and arsenic as well as traces of cadmium. The presence of titanium in significant quantities could explain the presence of titanium in the incinerator stack effluent although this element was not found at detectable levels in the dust samples taken. Some of the chromium found in Ponds 6, 7 and 9 (10) of the Gulf plant site may be natural in origin. However, the fact that it appears in concentrations up to about 30 times that in the soil supports the belief that much of the chromium in the ponds came from the chromium salts used for corrosion prevention in the cooling water system. This is supported by the results of an analysis done on a sample of wood taken from the cooling tower at the Gulf plant. As can be seen in Table V-13, it contains on average approximately 1450 ppm of chromium showing that it had been exposed to significant concentrations of chromium salts.

It should be noted in Table V-2 that all three soil samples show the presence of arsenic. This is likely to occur naturally in this area and may not correlate in any way with the operations of the plant.

It will be noted also that the selenium content of all three soil samples was less than 0.5 ug/g or ppm in the areas where

Table V-13 Analysis of Wood from Cooling Tower, Gulf Pincher Creek Plant

Job Number: 5327
Company: Gulf Canada Resources Inc. Pincher Creek Gas Plant
Sample: Wood from Cooling Twoer PC-83-19
Date Sampled: April 20th, 1983

TABLE 1

METAL ANALYSIS

	p.p.m. by weight			
	A	B	Average	g/m^3 of Wood
Cadmium	0.57	0.75	0.66	0.07
Chromium	1323	1569	1450	145
Copper	12.5	13.0	12.8	1.3
Iron	1148	1353	1250	125
Lead	3.3	3.5	3.4	0.3
Manganese	16.3	20.0	18.2	1.8
Nickel	3.1	3.8	3.5	0.4
Vanadium	Not detected			
Zinc	720	866	793	79

Source: Agat Engineering Ltd., Calgary, TASK FORCE, 1984.

had been mercury spills in the operation of the plant and that the soil had been contaminated by this toxic element. The report by Monenco (13) deals with this matter in considerable detail.

The analyses of soil samples show the presence of very significant quantities of aluminum and iron (probably as their oxides). There are lesser quantities of titanium, zinc, copper, chromium, lithium and arsenic as well as traces of cadmium. The presence of titanium in significant quantities could explain the presence of titanium in the incinerator stack effluent although this element was not found at detectable levels in the dust samples taken. Some of the chromium found in Ponds 6, 7 and 9 (10) of the Gulf plant site may be natural in origin. However, the fact that it appears in concentrations up to about 30 times that in the soil supports the belief that much of the chromium in the ponds came from the chromium salts used for corrosion prevention in the cooling water system. This is supported by the results of an analysis done on a sample of wood taken from the cooling tower at the Gulf plant. As can be seen in Table V-13, it contains on average approximately 1450 ppm of chromium showing that it had been exposed to significant concentrations of chromium salts.

It should be noted in Table V-2 that all three soil samples show the presence of arsenic. This is likely to occur naturally in this area and may not correlate in any way with the operations of the plant.

It will be noted also that the selenium content of all three soil samples was less than 0.5 μg/g or ppm in the areas where

these samples were taken. The normal range for soil is from 0.01 to 2 ppm. It is apparent therefore that these soils are relatively low in selenium. In this connection, it is interesting to consider the analyses of soil samples which were taken to determine whether selenium, possibly associated with sulphur in the sulphur block, may have contaminated the soil on the plant site. It will be noted in Table V-4 that the pH of the soil taken from the control area to the west of the plant site and from a location on higher ground above the sulphur block was 7.4 while that of soil taken below the block was 3.2 showing the effects of oxidation of sulphur to sulphuric acid by means of microorganisms. The selenium content of the soil samples taken to the west and from above the sulphur block are both less than 0.2 μg/g indicating a possible deficiency of this element. The sample of soil taken from below the sulphur block shows 1.1 μg/g compared with values ranging from 0.06 to 0.26 μg/g for soils classified as having "medium" to "high" selenium content (15). This would suggest that the selenium level in the area below the sulphur block is approximately four times greater than normal. It may be necessary to consider this factor, in determining what reclamation procedure should be followed.

Analyses of Condensate Samples

The subject samples were analyzed to determine whether they might contain any significant quantities of heavy metals. In performing these analyses, it was necessary to vent the light ends to depressurize the sample and to concentrate the remaining condensate. Experience indicates that organometallic compounds are likely to remain with the

heavier material in the sample bomb so the effect of venting the light ends would be to increase the concentration of any metals detected.

The analysis for trace metals of Gulf Pincher Creek condensate after venting and concentrating the sample is shown in Table V-4. It will be noted that many of the metals, if present, are at concentrations below the detectable limit which is in most instances considerably less than 1.0 ppm. Elements found in somewhat higher concentrations include potassium at 3.35 ppm, sodium at 1.92 ppm, mercury at 0.10 ppm, nickel at 0.95 ppm and silicon at 0.06 ppm. Later work (Appendix A-2) indicated that the value given for nickel was in error, the peak being caused by the xylene matrix used in the analysis procedure. Nickel is therefore not present in significant quantities.

The presence of the sodium and potassium is unexpected, but may have resulted from the condensate having been in contact with the produced sour water which contains significant quantities of both of these elements. The same explanation, to a lesser degree of certainty, holds true for the silicon found.

The mercury present at 0.10 ppm may be of concern if the condensate were being burned and the vapors were being released to the atmosphere or if considerable quantities of the condensate had been spilled and the mercury were allowed to concentrate as a residual. This matter is discussed again later.

The analyses of condensate from Shell Waterton Sheet 3 are given in Table V-5. Again, most of the elements for which

analyses were made were at concentrations below the detection limit. Those which were not included the following:

Barium	0.09 ppm	Copper	0.02 ppm
Potassium	3.67	Nickel	0.80
Sodium	2.13		
Selenium	2.77		

Again the presence of the potassium and sodium may be explained as indicated in reviewing the previous analysis. As before, it was shown that the nickel analysis was in error as described above and that nickel is not present in significant quantities. The fact that selenium was found at 2.77 ppm is interesting. In view of its chemistry being similar to that of sulphur, it is not surprising to find it occurring in a formation in which there are larger quantities of sulphur as hydrogen sulphide. The presence of copper at 0.02 ppm is also not surprising in view of the fact that there are known bodies of low grade, copper-containing ore at the surface above the gas field.

The results obtained from the analysis of Sheet 4 condensate (Table V-6) show the presence of the following elements at concentrations above the detectable limit.

Calcium	4.96 ppm	Cadmium	0.03 ppm
Iron	3.86	Copper	0.05
Potassium	3.12	Mercury	0.18
Manganese	0.03	Magnesium	0.30
Sodium	6.74	Nickel	0.81
Selenium	13.75		

Of the above list only selenium, cadmium, copper and mercury are of concern as toxic metals (nickel again is ruled out and

not considered present). The selenium, if burned as part of the condensate, would be emitted as selenium oxide and would help to replace a deficiency of this element known to exist in the area. The copper and cadmium would also appear as oxides in the emission from the stack if the condensate were burned. Since both of these elements are present in the soil in the area, it is not thought that their presence in trace quantities in the condensate constitutes a hazard. The mercury is of some concern but is also present in the soil at very low concentrations judging by the analyses of the soil samples. Soil analyses show no significant variation in mercury levels in the soil samples taken for the study. This suggests that there has been no accumulation of mercury in the area as a result of plant operations.

The composition of the condensate is of some interest as a possible source of the organic compounds detected in the ambient air downwind from the Shell plant.

Appendix A-4 provides an analysis of the condensate as obtained at the Shell Waterton plant. If one compares the organic compounds identified in the atmosphere downwind from the plant (See Table V-14) with compounds present in the condensate it will be noted that benzene, methyl benzene, ethyl benzene, 1,3-dimethylbenzene, C_3 benzenes, C_8, C_9, C_{10} and C_{11} hydrocarbons are present in both. The aromatics content of the condensate amounts to 12.3% of the total, while the naphthenes, normal paraffins and branched chain paraffins represent 6.9, 39.6 and 41.2%, respectively, of the total. All of these compounds should, if completely burned, produce harmless carbon dioxide and

water on passage through the flare. Those compounds associated with the trace quantities of metals in the form of organometallic compounds would burn to produce oxides of these metals in addition to carbon dioxide and water.

Analyses of Pentanes Plus Samples

The analyses for metals present in two "Pentanes Plus" samples taken from the Shell Waterton plant are shown in Table V-7 and V-8. These analyses were done on material taken from the sample bomb after depressurizing to atmospheric pressure, removing 300 ml of the liquid present and concentrating it to 50 ml under low heat. Since any organometallic compounds which are present are likely to be less volatile than the corresponding organic compounds, most of the metals in the 300 ml samples would be concentrated in the 50 ml samples which were analyzed. The concentrations of metals given in Tables V-7 and V-8 could, therefore, be higher by a factor of approximately 6 than the material in the "Pentanes Plus" collected at the plant.

In Table V-7 it will be noted that for sample 1, the concentrations of the following elements were below the detectable limit of the analytical method: silver, arsenic, calcium, chromium, iron, manganese, tin, vanadium, cobalt, thallium, gallium, antimony, indium, aluminum, beryllium, cadmium, copper, mercury, magnesium, molybdenum, lead, titanium, lithium, germanium, scandium, strontium and tellurium. Those elements detected as present, and their concentrations (ppm) in the concentrate, were as follows: barium (0.08), potassium (3.60), sodium (2.21), phosphorus (1,80), selenium (1.30), boron (0.2), nickel (0.9), silicon

(3.15), zinc (1.75). As discussed previously, the concentrations of nickel reported here are known to be in error. Nickel is not thought to be present at detectable levels. The remainder of the detected elements, if sent to the flare in combination with the organic materials with which they are associated, should burn and produce metal oxides in a finely divided state and in small concentration since they are present at parts per million levels ranging from 0.08 for barium to 3.60 for potassium. None of the oxides in this group is known to be toxic in this state.

The analysis of the second sample of "Pentanes Plus" with respect to its content of metallic elements is shown in Table V-8. The results are very similar to those of the first sample described above. The elements at concentrations below the detectable level in this case include: silver, arsenic, barium, calcium, chromium, manganese, tin, vanadium, cobalt, thallium, gallium, antimony, indium, aluminum, boron, beryllium, cadmium, copper, mercury, magnesium, molybdenum, lead, titanium, lithium, germanium, scandium, strontium, tellurium. This list includes barium and boron at undetectable levels in contrst to the previous list, and it does not include iron. Elements detected and their concentrations (ppm) were: iron (0.90), potassium (2.90), sodium (1.86), phosporus (2.10), selenium (8.08), indium (less than 1 ppm but detected), nickel (0.69), silicon (3.16) and zinc (2.04). Again the nickel is considered to be in error and not likely to be present in a detectable amount. The oxides of these elements, if produced on combustion of a portion of this stream in the flare or if spilled on the soil, would be in a finely divided state and in small quantities since as in the previous sample, they are present

in low concentrations ranging from 0.90 ppm for iron to 8.08 ppm for selenium. The latter may help to counterbalance the deficiency of selenium in the soil in the area, if it is in a form which can be utilized by vegetation.

Table V-9 shows the analysis of a benzene-toluene sample which had been stored in a stainless steel bomb for several days. It was thought that traces of the metals detected in the "pentanes plus" might possibly be "picked up" by the solvent action of the "pentanes plus". The analysis of the benzene-toluene showed potassium, sodium and nickel at levels above the detectable limit in each case. Since the presence of nickel was unexpected, a second blank sample of benzene and toluene was stored in another stainless steel bomb to check the result. At the same time, a portion of the benzene-toluene blank was stored for a period in a glass test tube. The results of the latter two analyses are given in Appendix A-2. The fact that nickel was detected at about the same concentration in the sample stored in the test tube as was detected in the sample which was stored in the "blank" bomb indicates that the method is in error for this element. The presence of the trace of sodium in the samples should not be surprising because the benzene-toluene had been stored in glass which may contain this element. It may be possible that potassium was derived from this source also.

Elements Present in the Produced Sour Water

The analyses of three samples of produced sour water for some 36 elements are given in Tables V-10, V-11 and V-12. These analyses are discussed below.

1. Gulf Plant Sour Water (Table V-10)

The sample of sour water obtained from the separator handling the stream produced by Gulf shows the following elements to be below the detectable limit for each of these elements: silver, selenium, vanandium, beryllium, tellurium, thallium, gallium, indium, scandium and germanium. Mercury was detected at 0.6 ppb (parts per billion), slightly below the Canadian drinking water standard. Barium, cadmium, cobalt, iron, manganese, sodium, tin, aluminum, chromium, copper, mercury, molybdenum, nickel, lead and zinc were detected at concentrations below 1.0 ppm. Cadmium, detected at a concentration of 0.13 ppm (verified by AA analysis), is 26 times greater than the 0.005 mg/L (ppm) maximum level established for drinking water standards.

Iron, manganese, chromium and lead are all somewhat higher than the maximum acceptable concentrations. Copper, zinc and arsenic are below the maximum acceptable concentrations.

The fact that this sour water contains 3200 mg/L (ppm) sodium indicates that the water is several times above the 500 mg/L (ppm) maximum acceptable concentration for total dissolved solids. This stream would therefore require very considerable dilution if it were to be released to a river. It would be preferable to follow Gulf's present practice of injecting it into a deep disposal well.

If this stream were collected in a pond and allowed to evaporate, the sediments would reflect the cadmium content present and may explain a portion of the cadmium found in samples taken in the flare stack area, the classifier area and the caustic burn-off area of the Gulf plant.

2. Shell Waterton Sour Water - Sheet 3 Formation Sheet, Table V-11.

Elements of possible concern with respect to health and aesthetic effects when present in drinking water include: silver, arsenic, barium, boron, cadmium, iron, chromium, lead and zinc. The concentrations of elements were below the maximum acceptable concentrations for drinking water in the subject sample. Manganese was slightly over the standard while mercury at 11.2 ppb was 11 times greater than the maximum acceptable value.

This analysis does not agree well with several analyses made of water taken from sludge catchers V-100 and VA-106 at the Waterton plant as shown in Appendix H-1. The latter samples contain several times as much calcium, potassium, magnesium, sodium and iron. It is thought that the sample on which the results in Table V-11 was based may have been diluted with water from condensed water vapor, causing the ion concentrations to be much lower than the concentrations observed in other samples.

The high levels of salt found in the samples indicated by analyses in Appendix H-1 (V-100 and VA-106) indicate

the need to dilute this stream intensively or to dispose of these waters via a deep disposal well. This would also solve the problem relating to the trace elements noted above.

3. Shell Waterton Sour Water - Sheet 4 Formation, Table V-12.

The concentration of cadmium in this stream (at 0.60 ppm by I.C.P. analysis and 0.95 ppm by AA Analysis) is 120-190 times the maximum acceptable concentration (0.005 ppm) for drinking water. Likewise, boron at 121 PPM is 25 times the standard for this element. Mercury and lead are approximately 3 and 5 times the standard respectively.

The high sodium content, 17,200 mg/L (ppm), causes a high total dissolved solids content making it desirable to continue the practice of injecting this stream into a deep disposal well.

Arsenic in this sample was found to be 14 ppm by ICP analysis. (A check by atomic absorption showed less than 10 ppb.) It would appear therefore that the trend towards lower concentrations of arsenic in the sour water effluent from production of gas from Sheet 4 observed in March and April 1983 must have continued.

The low levels of aluminum, copper, zinc, iron and titanium in this stream suggests that it was not the source of these elements found in the incinerator stack effluent by the Windsor Group.

ANALYSES OF THE AMBIENT AIR

Strosher and Parker of the Kananaskis Centre for Environmental Research surveyed approximately 40 sites in the Twin Butte area over an 11-day period using the mobile, trace sulphur gas analyzer. The results of this survey over the period October 18-28, 1983 are given in Table 15, page 43, Appendix A-1. Based on the results obtained, five sites were selected at which to take samples using "Tenax" adsorbent so that the materials collected from the sample of air in each case could be taken to the laboratory and analyzed on a GC-MS instrument. One of the sites was selected so as to provide a background sample and was therefore taken upwind, west of the plant near Well No. 19. The other four sites were selected at locations where sulphur containing compounds had been observed to be relatively high on the trace sulphur gas analyzer. The results of these analyses are given in Tables 10 through 14 of the report by Strosher (2).

Table 10, Appendix A-1 shows the analysis of the components absorbed from the air near Well No. 19. According to the analyses done with the trace sulphur gas analyzer, the concentrations of H_2S and SO_2 were too low to be detected in the first analysis while there was 3 ppb H_2S and no SO_2 detected in the second. (See analyses 27 and 28, Table 15, Appendix A-1.) In spite of these low and undetectable levels of H_2S and SO_2, the analysis done by GC-MS showed the presence of traces of 20 organic components. Nine of these components are the same, it will be seen, as those in samples taken downwind from the plant (Table V-14). Several of the components are the same as those found in condensate

Table V-14 Components Identified by GC-MS Analysis of the Ambient Air and of the Flare Stack Gases*

Ambient Air[a] Riviere Trailer	Ambient Air Hwy.6(Robertson's)	Raw Gas To Flare Stack	Acid Gas To Flare Stack	Sales Gas[b] To Flare Stack	Sales Gas To Flare Stack	Sulphinol Contactor Overhead to Flare Stack	Absorber Overhead To Flare Stack
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Carbonyl Sulphide	-	-	-	-	-	-	✓
Dichloromethane	Dichloromethane	-	-	-	-	-	-
-	C6 Hydrocarbon	-	-	-	-	-	-
Benzene	Benzene	✓	✓	✓	✓	✓	✓
Methyl Benzene	Methyl Benzene	✓	✓	✓	✓	✓	✓
Ethyl Benzene	Ethyl Benzene	✓	✓	✓	✓	✓	✓
1,3-Dimethyl Benzene	1,3-Dimethyl Benzene	✓	✓	✓	✓	✓	✓
Ethenyl Benzene	Ethenyl Benzene	✓	-	✓	✓	✓	✓
-	C8 Hydrocarbons	✓	-	✓	✓	-	✓
-	C3 Benzene	✓	✓	✓	✓	-	✓
Phenol	Phenol	-	✓	-	✓	✓	✓
C9 Hydrocarbons	C9 Hydrocarbons	✓	✓	✓	✓	-	✓
C10 Hydrocarbons	C10 Hydrocarbons	✓	✓	✓	✓	-	✓
C11 Hydrocarbons	C11 Hydrocarbons	✓	✓	✓	-	-	-

*Gases from various points in the plant are passed through a "knock-out" drum before going to the flare.

a) All samples except Sales Gas[b] passed over Tenax to absorb heavy components.
b) Gas sample collected in plastic sample bag.

Source: Kananaskis Centre for Environmental Research, TASK FORCE, 1984.

from the Waterton field, the analysis of which is given in Appendix A-4. One must conclude (a) that the atmosphere and soil in the area had been previously polluted by emissions from the plant flowing in a westerly direction and that the wind then shifted to the east leaving the components so that they were detected when sampling was done (b) that there was a leak from a pipeline or wellhead in the area or (c) that there had been a spill or leak of condensate in the area where the sample was taken. If there were very light winds at the time of sampling, it is also possible that some of these components may have come from the exhaust of the vehicle transporting the analytical instruments. Checks made on the wind speed and directions in the previous two days prior to sampling show that it was blowing from the west and southwest at speeds of 34 to 70 km/h (See Appendix A-3 for data supplied by Shell Canada Resources Ltd.) The fact that there was very little H_2S present in the area at the time of sampling suggests that it is unlikely that the components had been released from a pipeline or wellhead because gas in this area contains approximately 28% hydrogen sulphide. However, since hydrogen sulphide is more volatile than the other components detected, it will tend to escape more rapidly leaving the heavier, normally liquid components at ground level depending upon wind conditions and the turbulence of the atmosphere. The fact that the wind speed at the time of sampling (taken at the Shell Waterton plant) was 31 - 34 km/h would suggest that contamination from the vehicle exhaust was not likely. It is therefore concluded the hydrocarbons detected are from a leak or a spill of condensate in the area.

Another ambient air sample was taken at the Canwest Ranch, 19 km northeast of the Shell plant. The trace sulphur gas analyzer showed 4 ppb SO_2, indicating a downwind location with respect to the plant, and no detectable amount of H_2S. The GC-MS analysis (Table 11, Appendix A-1) shows some 23 components, six of which are identified to be the same as six found in ambient samples taken closer to the plant (See Table V-14).

Ambient air samples were taken on October 26 and 28, 1983 at the Riviere trailer site. Six identified components in the first of these samples were found present in the sample taken on October 28, at the same location (Table 14, Appendix A-1) and again in the sample taken at the Highway 6 site near Robertson's northeast of the plant (Table 13, Appendix A-1).

Several of the components identified in the ambient air sample on October 28, 1983 at the Riviere trailer site and on October 27, 1983 at the Robertson site (Highway 6) are listed in the first and second columns of Table V-14. In the first of these samples, carbonyl sulphide was detected indicating that carbonyl sulphide somehow escaped complete combustion in the incinerator or flare stack and appeared downwind.

It was also found that a peak corresponding to dichloromethane was detected in the sample taken on October 28, 1983 at the Riviere trailer site. This compound was also detected at the Robertson site on Highway 6. The source of this compound has not been identified. According to Mr. A. Mathes, Manager of Shell Waterton plant, no "freon-type" refrigerants are used in the plant so there must be another source of this material.

Other components found in common in the analyses of the two ambient air samples listed in Table V-14 include benzene, methyl benzene (toluene), ethyl benzene, 1,3-dimethylbenzene, ethenyl benzene (styrene), phenol and C_9, C_{10} and C_{11} hydrocarbons. The presence of styrene and phenol in ambient air samples taken downwind from the Shell plant and not in the sample taken upwind at Well #19 supports the contention that at least a fraction of the organic compounds detected downwind from the plant have passed through the flare stack. Styrene and phenol are not to be expected in raw gas from a well. Chemistry suggests that they are products of the chemical processes occurring in the oxidizing atmosphere of the flare. This evidence further supports the conclusion that the flare stack is not burning the waste gases discharged to it completely. To determine whether the flare might be the source of these components in the air, flare stack analyses were therefore undertaken. The results of these analyses will be considered later in this section of the report.

The results of ambient air monitoring given in Table 15 Appendix A-1, were obtained using the mobile trace sulphur analyzer. It will be noted that at 27 locations hydrogen sulphide (H_2S) was detected at levels ranging from 1 to 40 ppb. The ambient air standard for H_2S in this province is 12 ppb when averaged over a 30-minute period. Since the analyses represent single injections into the instrument, the average value over a 30-minute period or longer was not determined. It will be noted that all values higher than the standard were obtained on the plant site.

The presence of sulphur dioxide (SO_2) was detected 30 times in 49 samples. The concentrations determined ranged from 3

to 500 ppb. The Alberta ambient air quality standard for the province is 200 ppb averaged over a half hour period. Insufficient sampling was done to indicate whether this standard was exceeded. However, it is apparent that occasionally some significant peaks occur in the concentration of this component. It is considered unlikely that these peaks would arise from emissions from the incinerator stack since it operates under conditions of fairly uniform flow, with a long residence time and an excess of oxygen. It has sufficient height and thermal rise to prevent its plume from descending low enough to the ground to provide such concentrations of sulphur dioxide under most conditions. It is considered more likely that these sulphur dioxide peaks arise from the operations of the flare stacks. The matter will be discussed further in a later portion of this section.

It is interesting to note that in several instances, the samples taken west of the Shell plant and at Well No. 19 showed hydrogen sulphide but no sulphur dioxide. This is to be expected if the samples contain gas which has leaked from well heads or pipelines carrying the sour gas to the plant. The wind had been blowing strongly towards the plant for several hours (30 - 50 km/h) when these samples were taken so that the atmosphere in the sampling area would not contain SO_2 emitted by the plant.

Just why traces of H_2S were detected on three occasions at the Riviere trailer and road site when SO_2 was not detected is not clear. There might have been a leak of unprocessed gas into the atmosphere in that area or the wind may have

been coming from the direction of the prilling tower at the plant. In all other analyses done at this location the sulphur analyzer detected higher levels of SO_2 than H_2S again indicating that the gases being detected were associated with the operation of either the flare or the incinerator stack of the Shell plant. The fact that H_2S was found present along with the SO_2 supports the hypothesis that there might have been incomplete combustion of the H_2S in the flare. It is possible that some or all of the H_2S may have come from the prilling operation, but the contribution due to this source is likely to be small when SO_2 from the stack is being detected. The distance between the prilling tower and the flare stack (approximately 800 m) would reduce the extent to which the two plumes would merge by the time they reached the Riviere trailer site downwind.

Flare Stack Analyses Taken
When Various Plant Streams Were Vented

In an effort to determine the source of the many components detected in the ambient air downwind from the plant, permission was requested from the ERCB to flare five different gas streams from various points in the processing operations in the Shell plant for short periods. Fortunately, Shell has equipped its No. 2 plant flare stack with a line which can be maneuvered to sample gas which has passed through the flare flame. The gases are drawn through piping to the base of the flare stack by means of a steam ejector. Samples could then be pumped at a known rate for a fixed period of time over the Tenax adsorbent in a tube or

could be directed into a Tedlar sample bag so that the sample could be returned to the laboratory at the University of Calgary for analysis by the Kananaskis Centre for Environmental Research.

During the sampling operations it was noted that the flame of the flare was being blown almost horizontal by the stiff breeze (30 km/h) and that the tip of the flame sometimes extended over the sampling tube inlet. For this reason, it may be argued that combustion was not complete in the samples taken and therefore that the results do not truly represent the composition of the product gases being emitted into the atmosphere. However, when a comparison is made of the components identified in the samples taken from the flare with identified components found to be present in the ambient air downwind from the plant, one finds that several of the components match, suggesting that the combustion process in the flare flame was incomplete.

It should be pointed out that the gases which go to the flare from plant No. 2 all pass through a "knock-out" drum so that there is some contamination from one gas sample to the next from the liquids which collect in the drum. Nevertheless, very significant variations in the compositions of the different gases were observed indicating that the analyses do in part at least represent the various streams sampled.

It should also be mentioned that in normal operation, steam is added to the flare gases being combusted. This has the effect of preventing carbon formation in the flame as well as preventing polymerization of partially-combusted molecular fragments. During the tests of combustion of various plant

streams in the flare, the steam was shut off. The flame will burn hotter but will contain more carbon in the absence of steam. Because there was no dilution of the flame with steam, it should have burned more completely provided sufficient oxygen were available to burn the components present. Without good mixing to provide oxygen to the flame, one might expect incomplete combustion of the materials fed to the flame. In effect, under the conditions of the tests made, one would expect more complete combustion than when steam is added as under normal flaring conditions.

In Table V-14 the components identified by GC-MS analyses are presented for periods when (i) raw gas, (ii) acid gas, (iii) sales gas, (iv) sulphinol contactor overhead gas and (v) absorber overhead gas were sent to the flare. All of the gases sampled after combustion in the flare were passed over the Tenax adsorbent to adsorb the heavier components except for one case (sales gas in column (5)) in which the sample was collected in a Tedlar bag so that a comparison of sampling methods could be made.

In Table 3, page 9 of Appendix A-1, the results of analyses made for sulphur-containing gaseous components in the samples of effluent drawn from the flare with various streams from plant No. 2 being burned are given. Again it is not known whether or not the components detected might have been burned more completely had the sample been taken further downwind from the tip of the flame. While the H_2S, COS and CS_2 recorded could be further oxidized, the SO_2 is not likely to be oxidized further and if anything would likely increase as a result of the oxidation of the former three compounds.

If further oxidation of the H_2S detected did not occur, then one would expect to find H_2S along with SO_2 in downwind samples. As indicated earlier, this combination was observed in 12 samples taken at the Riviere trailer site.

1. Raw Gas to the Flare

From column (3) in Table V-14, it will be noted that there are 10 compounds in the sample taken from the flare which check (v) with compounds found in the two samples of ambient air (columns (1) and (2)) which were taken downwind from the plant. It is possible that there are other components which would match if some of the unknowns in the analysis could be "sorted out".

An examination of Table 7 in Appendix A-1, shows that in addition to the components listed in column (3) of Table V-14, other components such as carbon disulphide, dimethyl sulphide, 2-methyl thiophene and 3-methyl thiophene were detected in significant quantities. It is possible that they are normally largely consumed by the flame so that they would not be detected downwind in the ambient air samples, or that the sampling downwind was done when there was no flaring of this stream at the plant. Should any of these components survive the flare, however, they could add significantly to the odor of the flare plume downwind from the plant.

It will be noted that some 74 components (both identified and unknown) are listed in Table 7,

Appendix A-1 for combustion of the raw gas. They range in molecular weight from 78 for benzene up to 142 for 2-methyl naphthalene. One of the major components detected in this analysis was benzene, a known carcinogen. It should be pointed out that the method of analysis used is very sensitive, that complete combustion may not have occurred in the sample taken from the flare and that benzene as well as several other compounds detected are components of gasoline to which members of the public are exposed whenever a car's gasoline tank is filled. Nevertheless, the fact that ten of the compounds found in the flare stack sample match with compounds detected in the atmosphere downwind from the plant suggests that the flare stack was not combusting the waste gas completely.

2. Acid Gas to the Flare

In Table 8, p. 26 Appendix A-1, results of the analysis by GC-MS of the sample collected from the flare while acid gas was being burned are provided. It will be noted in column (4) of Table 5.14 that nine components were identified which correspond with components identified in ambient air samples collected downwind from the plant (Columns 1 and 2). Again this suggests that the components detected downwind in the ambient air may originate from incomplete combustion in the flare.

A review of the components listed as being present in the sample taken from the flare while burning acid gas (Table 8, Appendix A-1) shows the presence of

SO_2, CS_2 and 3-methylthiophene, as well as 44 other components. Compounds such as benzaldehyde, benzonitrile, phenol, naphthalene and many other combinations are present. These compounds may well be burned if the flare is functioning properly but the fact that some of the components e.g. phenol and 1,3-dimethyl benzene are being detected downwind suggests that this is not always the case.

Table 3, page 9 of Appendix A-1 shows that when acid gas was burned, the sample taken at the tip of the flare contained H_2S, COS, CS_2 and SO_2 at concentrations of 300, 35, 250 and 3000 ppm respectively. As indicated before, the first three of these components could oxidize further to add to the SO_2 level observed. The latter is likely to be dispersed as such. If indeed, the analysis above represents the end products of combustion in the flare, the proportion of H_2S and SO_2 present would suggest that the reaction was only approximately 90% complete.

3. Sales Gas to the Flare

In Tables 4 and 9 of Appendix A-1, the GC-MS analyses of samples collected from the flare when sales gas was being burned are given. The sample components given in Table 4 represent what was collected on a Tenax adsorbent while those given in Table 9 were injected into the instrument from a Tedlar sample bag. It will be noted that only 23 components were found with the Tenax adsorbent while 59 components

were detected with the sample bag. This difference may in part be due to the size of the sample injected into the instrument but may also reflect the inability of the Tenax to adsorb all of the lighter components in the conditions under which the sample was collected. It will be noted that this analysis shows the presence of a C_6 hydrocarbon which was not detected in other samples absorbed on Tenax. Also no COS, CS_2, dimethyl disulphide or other sulphur containing compounds were detected in this stream suggesting either that the carry-over of these components from one stream to the next due to retention in the knock-out drum is not great with respect to these compounds or that Tenax does not retain them under the conditions of collection.

It will be observed in columns (5) and (6) of Table V-14, that in each case, there were ten components identified which matched with those observed in the ambient air downwind from the plant. Again this suggests that the components detected downwind result from incomplete combustion in the flare. Analysis of the gases from the tip of the flare by the mobile sulfur-gas analyzer shows H_2S, COS, CS_2 and SO_2 at concentrations of 30, 13, 13 and 275 ppm, respectively. Here again the remaining H_2S is approximately 10% of the total of sulfur-containing compounds suggesting that the reaction was only approximately 90% complete.

4. Sulphinol Contactor Overhead Gas to the Flare

Table 5, page 19, Appendix A-1 provides the GC-MS analysis of the gas sample taken from the flare when gas from the sulphinol contactor was combusted. From Table V-14 it will be noted that six components identified in this gas sample correspond with components identified in the ambient air downwind from the plant. Sulphur dioxide was not identified in this sample although benzene at a relatively low concentration was detected. The largest fraction observed was due to the presence of naphthalene. Toluene (methylbenzene) and phenol were both present in small but significant proportions.

The analyses by means of the trace sulphur-gas analyzer shown in Table 3 (Appendix A-1) indicates the presence of H_2S, COS, CS_2, and SO_2 at concentrations of 100, 20, 75 and 700 ppm, respectively, considerably lower than the values seen when burning acid and raw gas but higher than those for sales gas, as might be expected. It will be noted again that the H_2S in the sample was approximately 10% of the total suggesting that the reaction was only about 90% complete with respect to H_2S combustion. Again, however, there is no positive proof of this because combustion may have been more complete than this analysis indicates.

5. Absorber Overhead Gas to the Flare

In column 8 of Table V-14 the GC-MS analysis of the sample of gas taken from the flare when overhead gas from the absorber was being burned is given. In this instance 11 of the components identified match with components identified in the ambient air samples collected downwind from the plant (columns (1) and (2), Table V-14). This serves to further reinforce the evidence that the components detected downwind from the plant occur as a result of incomplete combustion of waste gases sent to the flare during times of plant upsets. It was interesting to note that carbonyl sulphide (COS) was detected in this sample; this product is formed in the combustion process. Its presence in the ambient air (Column 1, Table V-14) can therefore be associated with operation of either the incinerator stack as indicated earlier, or the flare as suggested here.

The analytical results are given in Table 6, page 21, Appendix A-1 for this sample. In addition to carbonyl sulphide, carbon disulphide and 3-methyl thiophene were detected. Again, benzene was found to be one of the components present in a significant fraction. Benzaldehyde, phenol and naphthalene also appeared in minor proportions.

The concentrations of H_2S, COS, CS_2 and SO_2 detected in the sample taken from the flare and analyzed on the trace sulphur gas analyzer are given in Table 3, page 9 of Appendix A-1. The values were

275, 50, 290 and 1460 ppm, respectively. A comparison of this analysis with that of the sample taken when raw gas was being flared suggests that COS should have been detected by the GC-MS method, since the COS concentration found in the combustion of the raw gas was almost double that found in the analysis of the sample under consideration. The several sulphur-containing compounds found in the analysis of the raw gas burned in the flare may have masked the detection of COS.

The concentration of unconverted H_2S in the sample as taken suggests that the reaction was only approximately 85% complete but again the sampling method may be questioned.

GENERAL DISCUSSION

If one assumes that the Shell-Waterton plant was running in approximately the same manner when the analytical work described above was done as it was when Strosher did similar analyses in August and September of 1981, then the quantitative results given in his report of that work (3) may be used in conjunction with the more qualitative work of the present report. Strosher found benzene concentrations in the ambient air ranging from 0.005 to a maximum of 16.3 g/m^3 (5 ppb). The latter value was obtained at a point about 200 metres east of the Shell plant site and probably represents fugitive or flare stack emissions. This concentration is 2000 times smaller than the amount of benzene allowed in the workplace by the National Institute for Occupational Health in the United States (20). This would suggest that there is little

to be concerned about with respect to this component in the air downwind from the plant. In support of this view, it has been noted that a recent ambient air survey done in the fall of 1981 in Los Angeles showed benzene concentrations ranging from 12 to 29 ppb (18) in that city. Relative to Strosher's value these values are high; however, one cannot be sure that the level detected by Strosher represents a maximum value.

If instrument responses to SO_2 and benzene are assumed to be equal, then Table 4 (Appendix A-1) shows that fairly significant and approximately equal fractions of SO_2 and benzene are present in the products from the flame when sales gas is burned. Table 9, Appendix A-1, shows the analysis of gas collected from the flare in a Tedlar bag when sales gas was burned. This analysis also shows significant SO_2 and benzene peaks of about equal magnitude, as was the case with the previous sample. The fact that the SO_2 concentration detected by the mobile sulphur gas analyzer showed a concentration of 275 ppm (See Table 3, Appendix A-1) suggests that benzene at about this level was being emitted by the flare when these samples were taken.

Calculations of the downwind concentration of benzene, assuming that this concentration leaves this stack during flaring of sales gas, results in a much lower concentration of benzene in the ambient air than the maximum value observed by Strosher (3).

The question which naturally arises is, why are compounds such as benzene present in the flare gas products when sales gas which contains virtually no benzene is flared? Also, why are these organic components present in the flare gas

products when gases from other points in the plant are flared? The correspondence seen in the compounds detected in the air (Table V-14) when matched with compounds known to be present in condensate (Appendix A-4) shows that portions of the latter must be carried through the plant to the knock-out drum installed immediately upstream from the flare. Here the volatile condensate liquids are trapped and whenever gases from various points in the plant are flared, they pass through the knock-out drum contacting the condensate and carrying with them some of the volatile condensate compounds. If they are not completely combusted by the flare they will appear in the atmosphere downwind from the plant. On consideration of the information available, the concentrations of the condensate components detected in the ambient air do not appear to be high enough to be of concern based on published threshold limit values for the various toxic compounds which have been detected (5).

A recent article has taken a rather different point of view on ambient air quality. In the opinion of Professor R. E. Albert of the Institute of Environmental Medicine, New York University Medical Center (19), the threshold limit value for benzene, i.e. 10 ppm for workers on an 8-hour per day work schedule, should be reduced by a factor of 100 in considering the outdoor environment. This would allow a factor of 10 for the possibility of other potentially harmful compounds being present, and another factor of 10 because susceptible people such as children and those less healthy than industrial workers may be exposed on an "around-the-clock" basis. The resulting value of 0.1 ppm suggested for benzene in the atmosphere would still be 20 times greater than the maximum value determined by Strosher(3).

Other questions arise which should be considered. Could people be exposed on an "around-the-clock" basis and could there be higher concentrations than Strosher observed? Technically, flaring should occur for short periods and the probability is high that a wind would carry the pollutants away, causing dilution with the passage of time, so that the people living downwind should not be affected. There is, however, the possibility that a short period of flaring might be followed by a relatively calm period in which the polluted air would linger in the area downwind from the plant. It has been estimated that the half life of benzene in the atmosphere is three days (19) and therefore if a calm period prevailed (a rather unlikely scenario in this area) traces of organics might also prevail. Whether the trace concentrations of organic compounds, such as benzene, could rise above the levels determined by Strosher is not known; it is considered unlikely that they would increase by a factor of 20. It is recommended, nevertheless, that further checks be made on the trace concentrations of organic compounds in the air under the adverse conditions described above, to determine whether indeed the concentrations of these compounds could possibly approach levels at which there would be cause for concern.

In the above discussion, benzene was emphasized because information is available regarding its toxicity and half life in the atmosphere. A number of other components identified in the atmosphere downwind from the Shell plant are also considered to be toxic pollutants. Based on standards published by the American Conference of Governmental Industrial Hygienists (20) the threshold limit values for

these components are given below for people exposed in the workplace for eight hours per day.

Table V-15 Threshold Limit Values for Certain Compounds

Threshold Limit Values Compound	Concentration ppm (Volume)	$\mu g/m^3$
Benzene	10	30,000
Methyl benzene (toluene)	100	375,000
Carbon disulphide	20	60,000
Hydrogen sulphide	10	15,000
Ethyl mercaptan	0.5	1,000
Ethyl benzene	100	435,000
Naphthalene	10	50,000
Phenol	5	19,000
Styrene	100	420,000
Sulphur dioxide	5	13,000
Trimethyl benzene	25	120,000

Source: American Conference of Governmental Industrial Hygienists

These values are permissible upper limit concentrations of these compounds allowed in the design and operation of laboratories and workplaces. The value given for sulphur dioxide is 500 times the "annual, maximum desirable arithmetic mean value" of 0.01 ppm and 25 times greater than the specified "maximum desirable average reading" over a half-hour period taken downwind from a sour gas plant in the Province of Alberta. The value given for hydrogen sulphide is 3300 times the specified 24-hour maximum desirable value for Alberta which is 0.003 ppm. The limits set on these two pollutants were arrived at for reasons other than health but make the factor of 100 proposed by Professor Albert appear conservative by comparison. Certainly the number of toxic materials detected in the ambient air downwind from the Shell plant support the approach taken by Professor Albert.

The following statement taken from a text by Crawford (17) indicates the nature of the problem and reinforces the need for care being taken in considering what might be reasonable concentrations of pollutants in the environment.

"For atmospheric environments, definitive standards have not been published yet. However, in most cases the maximum limits of pollutant concentration in atmospheric air will certainly be considerably less than the values listed in Table 1.1.* There are several reasons for this: First, the allowable limits for industrial workers are based primarily on the long-term toxic effects of different concentrations for which no detrimental effects are believed to occur. For the population as a whole, however, the nuisance value of pollutants is as significant in setting the limits as is the health value, at least if the nuisance value results in a lower limiting value. Second, members of the general population are exposed to pollutants for a much longer period of time than industrial workers in a normal work week. Third, some members of the general population are in a much worse state of health or are more delicate as are children, than are most industrial workers, and for them exposure to very high concentrations of certain pollutants could be a direct cause of death or serious illness. Fourth, different substances present in a polluted atmosphere react with each other in the presence of sunlight to form highly complex compounds, many of which may have harmful toxic effects that the original pollutants might not have. These reactions can take place with very low concentrations, and so

*The preceeding Threshold Limit Table is a partial listing of the reference Table 1.1.

for this reason also the allowable concentrations in the atmosphere will probably be quite low."

In view of this situation it would seem prudent to attempt to reduce the concentrations of the organic compounds detected in the ambient air if it is reasonable to do so.

Operation of the Flare Stack

The flare stack used to burn waste gases from plant No. 2 at the Shell Waterton site is 63.1 m tall and was designed to disperse the sulphur dioxide emitted during flaring operations to meet governmental regulations. Sweet gas is added to the raw gas or other sour gas being flared in ratios of 1:1 to 2:1 to cause additional thermal lift and to dilute the sulphur dioxide in the plume produced (21). The cost of burning sweet gas should serve to minimize the duration of such flaring operations and, therefore, to reduce the times over which pollutants may be released at concentrations which approach "maximum desirable" standards at ground level downwind from the plant. Downwind monitoring is undertaken to record whether the concentrations of sulphur dioxide exceed the values set down in the regulations.

It should be recognized that operation of flare stacks is far from ideal. They must be operated with widely varying waste gas feed rates and with varying feed compositions. The mixing of the air with gases being discharged may be inadequate to ensure complete combustion. The stack associated with the No. 2 plant at the Shell-Waterton site is located in a ravine which is subjected to very high winds, largely from the west and south west. These winds tend to

reduce the extent of the rise of the plume and may possibly cause downwash of the plume into vortices created immediately downwind from the stack under high wind conditions. If this phenomenon were to occur, it would tend to increase downwind concentrations of pollutants such as sulphur dioxide. The fact that it is necessary to add sweet gas while flaring raw or sour gas through this flare indicates that its operation is borderline with respect to the standards set down by the government.

Recently, an article by Hackney et al.(23), indicated that there can be "significant increases in airway resistance" of moderately exercising asthmatics who are exposed to as little as 0.25 ppm of sulphur dioxide for 10 minutes when using a mouthpiece breathing device. Even natural breathing of sulphur dioxide can cause some asthmatics to experience increased airway resistance with as low as 0.4 ppm SO_2 with heavy exercise. The effects resolve quickly with rest even in the atmosphere of the test.

In view of the above findings with respect to asthmatics, it becomes apparent that every effort should be made to prevent SO_2 concentrations at ground level downwind from the plant from increasing above the standard significantly even for periods of a few minutes.

Possible Solutions To The Problems

The presence of traces of organic compounds which have been detected from time to time downwind of the Shell plant is related to the incomplete combustion of compounds present in

condensate which are carried into the flare. It may be possible to solve this problem by operating the plant so that at all times there is a minimal amount of condensate in the knock-out drum. Such material might be recycled so that the condensate being carried to the "knock-out" drum could be recovered for sales.

Although it may be possible to prevent compounds present in the condensate from reaching the flare, two other problems remain. Unless there is complete combustion in the flare, odoriferous components such as H_2S and other sulphur-containing compounds are still likely to cause odor problems downwind from the plant. Redesign and perhaps relocation of the flare stack may help to increase the extent of combustion and the dispersion of waste gases. Such measures, however, will not completely solve the problem due to the emission of SO_2 whenever it is necessary to use the flare. This is especially true when raw gas and acid gas, which contain substantial portions of hydrogen sulphide, are flared. Consideration should be given to methods of operation which would avoid the use of the flare. If this is impracticable, it may be possible to reduce the extent of flaring by changes in the operating procedure of the plant. Such proposals might have some economic benefit because of the gas saved as well as helping to solve the pollution problem created by the flare.

CHAPTER SIX

CONCLUSIONS

This chapter summarizes the main conclusions agreed to by the Task Force regarding air, soil and water quality in the Twin Butte area.

GENERAL CONCLUSIONS

In reviewing the overall impact of air, soil and water quality in the Twin Butte area, the Task Force has concluded that:

1. Based on the analytical evidence available, (Monenco Report) toxic materials are present in the ponds, in landfills and in areas actively used during the Gulf plant operations. The Task Force study indicates that, with minor exceptions, these substances are contained within the boundaries of this plant site.

2. Preliminary reconnaissance conducted by the Task Force at the Shell plant site identified the presence of sulpholane and $C_7H_{11}NO_3$ in the groundwater. Sludges in the tested ponds did not contain substantial quantities of trace metals. No soil survey at this plant was conducted.

3. No evidence was found that heavy metals or toxic substances in substantive quantity, originating from gas processing, have migrated from the plant sites. The exceptions to this statement were:
   - Mercury levels at piezometer (20-1) at the Gulf Pincher Creek plant were observed to be slightly higher than background levels.
   - Arsenic levels exceeding drinking water standards were identified in early 1983 at the discharge point from the Shell Waterton plant into the Drywood Creek.

SURFACE WATER AND GROUNDWATER HYDROLOGY

The impact of the Shell Waterton and Gulf Pincher Creek gas plants on water quality in the Twin Butte area have been reviewed thoroughly. The Task Force has concluded that:

1. Effluent quality of the plants generally complied with the Process Effluent Standards established by Alberta Environment. According to the records of the Pollution Control Division, occasional contraventions of the following parameters were observed: Gulf Pincher Creek - chemical oxygen demand (COD), total sulphide, oil and grease, threshold odor number, lead and mercury; Shell Waterton plant - arsenic, zinc, cyanide and ammonia.

Effluent from the Shell Waterton Gas Plant causes an increase in total dissolved solids, main ions, nutrients and some trace element concentrations in the North Drywood Creek and Drywood Creek. The Gulf Pincher Creek Gas Plant has ceased operation; however, it is reasonable to conclude that, in the past, effluent discharge from the Gulf plant had similar downstream effects to those observed at the Shell plant.

With the exception of North Drywood Creek and Drywood Creek, no other creeks or lakes in the area have water quality distinctly affected by the Shell and Gulf plant operations.

2. The environmental isotope studies indicate that the surface water system is hydraulically continuous with the shallow groundwater system and that recharge is rapid in geological terms. Available results indicate that there is no evidence that the groundwater quality is affected by the sulphur emitted from the gas plants.

In general, the surface water and shallow groundwater of the Twin Butte area are affected by the process of evaporation/concentration. This process is indicated by the enrichment of stable isotopes in groundwater and the presence of moderately saline sulphatic surface water in the lakes.

3. Groundwater quality in the wells located in the areas adjacent to the Shell and Gulf plants does not indicate the presence of anomalies which could be attributed to industrial pollution. The only exceptions to this statement are the anomalously high values of total dissolved solids and sulphates in the area extending SE of Gulf's Pond 8 and in the spring water below the Shell plant in the North Drywood Creek Valley.

4. Localized zones of groundwater contamination are present at the Shell Waterton and Gulf Pincher Creek plants. High total dissolved solids and sulphate concentrations are prime indicators of groundwater contamination. At the Gulf plant, anomalous concentrations of trace elements and organic compounds, which could be attributed to the plant operation, were detected. Sulpholane, an essentially non-toxic chemical used in sour gas processing, was found in concentrations up to 100 ppm in groundwater at the Shell Waterton plant.

5. The most important observations based upon the geochemical weathering tests of six till samples from the Twin Butte area are:

   a) that a threshold partial pressure exists below which there is little or no reaction of SO_2 with an aqueous suspension of soil/till, and
   b) that the release of trace metals can occur only if the pH of the soil-water system falls below 3.0 approximately. The threshold value of the partial pressure of SO_2 lies between 34 ppm and 3400 ppm for the materials studied. Increasing amounts of

organic carbon, calcium, sulfate, silica, copper, lead, cadmium, cobalt, nickel, manganese, vanadium, chromium, strontium, aluminium, and zinc were released upon exposure of a shallow till with sample to 0.34 percent SO_2 by volume. The trace metals released were not at toxic levels, even at a pH as low as 2.4.

6. Process water and surface runoff ponds at the Gulf Pincher Creek and Shell Waterton gas plants contain fresh to brackish water of similar main ion composition. Concentrations of trace elements in the ponds at the Gulf plant are higher by a factor of ten or more in comparison with the corresponding ponds at the Shell plant. In general, concentrations of trace elements in the Gulf ponds exceed background concentration levels.

7. Surface water quality in the creeks flowing through the study area exhibit seasonal variations expressed by different concentrations of ions.

8. Groundwater chemical composition in the study area varies within a wide range from fresh to brackish water representing a number of different hydrochemical types. In terms of total dissolved solids and variation in chemical composition, the water samples collected in the study area are quite typical of evaporative surface water impoundments and shallow groundwater in other areas of Alberta covered by till containing carbonates and organic-rich shales.

   With the exception of iron and manganese, the trace constituents were not found in groundwater at

concentrations that exceeded the maximum acceptable for drinking water.

9. The hydrochemical data assembled and evaluated in the Task Force study originate from other studies and sampling programs. In some instances, the lack of descriptions of sampling, preservation and analytical methods made proper evaluation of the results difficult.

ANALYSIS OF SOIL AND VEGETATION

The Task Force has reviewed the data and concludes that:

1. Sulphur, presumably as SO_2, has been air borne in the direction of a) the Drywood Creek valley at least as far as the Waterton reservoir, b) the Pincher Creek valley as far as Daigle Lake and possibly c) the Foothill Creek valley as far as Rouleau Lake.

2. There has been no detectable increase in acidity or electrical conductivity of soil, litter and lake sediment in these areas, concomitant with a readily detectable increase in ^{34}S.

3. Equally, there has been no detectable, concomitant increase in concentrations of metals in soil, vegetation or lake sediment in these areas.

4. There was no indication of any increase in concentrations of metals in potatoes and carrots grown in 1983 in the study area, as a result of gas plant operations. The vegetables obtained were safe to eat.

5. There were indications of contamination with chromium, lead and zinc of bullrushes downslope from settling ponds at the Gulf Pincher Creek plant, possibly because of surface run-off.

GASEOUS AND PARTICULATE EMISSIONS

The Task Force has reviewed the data and concludes that:

1. The organic compounds detected in trace amounts in the ambient air were a result of flare stack emissions.

2. Gases directed to the flare stack during the tests contacted condensate, a volatile liquid fraction produced from the raw gas, which was trapped in a "knock-out" drum immediately upstream from the flare.

3. Condensate may be carried into the flare when gases from various points in the plants are flared. Combustion of this condensate was incomplete, under the conditions of the tests undertaken, giving rise to the presence of the organic compounds detected in the ambient air downwind from the plant.

4. The trace element emissions from the incinerator stack detected by the University of Windsor Group probably came from the soil and dust picked up by the wind which were then carried through the reaction system.

5. The Shell plant finds it necessary to add sweet gas to sour gas when the latter is being flared to achieve greater thermal lift and to decrease

concentrations of sulphur dioxide at ground level to values less than the standards set for ambient air quality. It is therefore concluded that when flaring occurs, the sulphur dioxide levels downwind from the flare stack will tend to approach the upper limits of the standard. Insufficient dilution of the sour gas with sweet gas, coupled with adverse dispersion conditions, could cause ambient sulphur dioxide levels to exceed the standard for short periods.

CHAPTER SEVEN

RECOMMENDATIONS

This chapter summarizes the recommendations which have been made following detailed review of findings and conclusions regarding air, soil and water quality in the Twin Butte area.

SURFACE WATER AND GROUNDWATER HYDROLOGY

The Task Force recommends that:

1. A further survey of groundwater and surface water should be conducted to determine the presence and concentrations of organic compounds near the Shell Waterton plant. This recommendation follows from the detection of sulpholane in shallow groundwater, and accommodates the possibility of air-borne contamination of surface water. Groundwater samples should be subjected to a standard fish toxicity test.

2. The monitoring of surface water, spring and observation wells at the Shell Waterton plant should be continued. Additional piezometer nests should be added in the areas of Basin A, Plant #2 Slurry pond and Basin K. A detailed survey of the solid waste disposal sites should be conducted and an appropriate groundwater monitoring system established.

3. The reclamation program developed by Gulf should be implemented and progress of the work monitored by the owner and by government agencies. Since the Pincher Creek plant was the first major sour gas plant built and the first to be closed in Alberta, the experience gained in site reclamation should be used to establish appropriate guidelines for operating and decommissioning similar plants. Additional piezometers should be installed and isotope studies conducted to define the origin of the hydrochemical anomalies SE of Pond 8 in the upper and lower aquifers. Piezometer 29-1 should be resampled and mercury concentrations in the groundwater confirmed. Groundwater samples should also be monitored for contamination by organic compounds.

4. Detailed hydrological and hydrogeological studies (including application of environmental isotopes) should be conducted, prior to any new sour gas plant construction. This would provide hydrochemical baseline data, which may be required in the future for environmental impact assesments. Standards or guidelines should be established for operating and decommissioning of the plants.

5. Procedures for water sampling, preservation and transportation to be used in all hydrochemical studies should be established. Analytical methods for different ions or compounds should be recommended. The present use of methods with different levels of accuracy make the evaluation and comparison of the results very difficult.

6. The results of the artificial weathering tests in an SO_2 atmosphere indicate great potential for this method in future studies related to sour gas plant operations. Further studies should be conducted to define the sensitivity of different soils in Alberta to sulphur loading and release of trace elements. This study should also include evaluation of the potential impact on groundwater quality of sulphur dust deposition on the ground surface.

7. Water stored in ponds on the Gulf Pincher Creek plant site contains high concentrations of different trace metals. It should not be released to the surface drainage system without appropriate treatment.

8. Further study is recommended to develop suitable techniques for the sampling and interpretation of data regarding atmospheric chemical composition. The Task Force has shown potential for the use of this method in delineating areas affected by sour gas plant emissions.

9. The effects of SO_2 emissions and sulphur dust deposition on snow cover should be investigated to determine the potential for generating acid snow-melt run-off.

ANALYSIS OF SOIL, VEGETATION AND SEDIMENT

The Task Force recommends that:

1. After an appropriate time interval (5 years?) measurements of ^{34}S values in soils, vegetation and lake sediments should be repeated to establish whether an equilibrium has been reached or whether ^{34}S values are still increasing to more positive levels. This may indicate whether potentially damaging effects of air-borne sulphur deposition have reached a plateau. A more detailed sampling would also confirm whether or not this air-borne sulphur actually follows the valleys of the Drywood, Pincher and Foothill Creeks.

GASEOUS AND PARTICULATE EMISSIONS

The Task Force recommends that:

1. The placement, design and operation of the flare stacks should be reviewed and efforts made to ensure the most complete combustion, that is technically feasible, of the waste gases sent to the flare stacks of the Shell Waterton plant specifically and any other plant under study.

2. The condensate trapped in the knock-out drum immediately upstream from the flare stack should be kept at the lowest possible level so that gases being flared carry as little condensate as possible to the flare.

3. Plant operating procedures should be reviewed with the objective of eliminating the need for, or reducing the extent of, flaring within technically feasible limits.

4. In addition to monitoring the ambient air for sulphur dioxide and hydrogen sulphide, analyses should be made when flaring is taking place to determine whether the concentration of organic compounds in the ambient air downwind from the plant reach levels which might be considered hazardous to the health of people living in the area.

5. Future studies of the effects on animal health of compounds added to inhaled air should include the organic compounds found in ambient air near the Shell plant as well as sulphur compounds such as SO_2, H_2S, CS_2 and COS.

GENERAL RECOMMENDATION

The Task Force recommends that:

1. The operators of these and other sour gas plants should take steps to maintain closer liaison with residents of local communities through such things as joint committees, newsletters, etc., to avoid misunderstanding and animosity that compromise efforts to achieve an objective appraisal of the effects of sour gas processing.

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EXECUTIVE SUMMARY

TWIN BUTTE

SOILS AND WATER EVALUATION

TASK FORCE

AUGUST, 1984

August 3, 1984

HON. FRED BRADLEY
Minister of the Environment
Legislative Buildings
Edmonton, Alberta

Mr. Minister:

We take pleasure in submitting the EXECUTIVE SUMMARY of the TWIN BUTTE SOILS & WATER EVALUATION TASK FORCE. We have also attached a TECHNICAL REPORT and the technical appendices to this report in separate volumes for future reference.

Respectfully,

Hilton R. Pharis,
Chairman

Dr. Eric Tollefson

Ben Zukiwsky

Dr. Tadeusz Dabrowski

Bob Clark

Dr. John Ashworth

Wendy Carpentier

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CHAPTER ONE

INTRODUCTION

The Twin Butte Soils and Water Evaluation Task Force was appointed by Ministerial Order of the Hon. Fred Bradley, Minister of Environment on April 28, 1983. The Task Force was made up of the following members:

- Mr. Hilton Pharis, Chairman;
  A rancher and Reeve of the Municipal District of Pincher Creek.

- Mr. Ron Zukiwsky;
  School Principal and Pincher Creek Town councillor.

- Mr. Bob Clark;
  Former member of the Legislature for Olds-Didsbury.

- Mrs. Wendy Carpentier;
  An area resident and President of the Pincher Creek Industrial Pollution Committee.

- Dr. Eric Tollefson;
  Professor of Chemical Engineering, University of Calgary.

- Dr. Tadeusz Dabrowski;
  A Calgary hydrogeologist with the firm of Piteau and Associates.

- Dr. John Ashworth;
  A soil chemist with Norwest Soil Research Ltd. in Edmonton.

The Terms of Reference of the Task Force as outlined by the Minister of Environment were:

1. determine the nature and level of substances which are contained on the Gulf Pincher Creek and Shell Waterton gas plant sites resulting from the gas plant operations;
2. determine if any surface or sub-surface migration of these substances off of the plant site areas has occurred and the extent thereof.

The Task Force was also directed to conduct an independent study to evaluate the Gulf Canada report which identified heavy metals and organic compounds on the Gulf site.

The study area included:

- the populated areas immediately surrounding the Shell Waterton and Gulf Pincher Creek Plants
- the rural areas of Glenwood, Hill Spring and Twin Butte.

The objectives of the Task Force were established through a series of meetings with concerned citizens, visits to the plant sites and reviews of the existing reports regarding the soil and water on both plant sites. Following this process, the committee developed and conducted a research program that met the Terms of Reference set out for the Task Force.

Surface migration was discussed at length by the committee and taken to include the gaseous particulate emissions leaving the incinerator and flare stacks of the plants as well as particulate and gaseous matter carried by the wind from above the plant site. The Minister of Environment was advised and agreed with the intentions of the Task Force to include this concern in its mandate.

The Task Force outlined a program to be conducted by consulting and research organizations, coordinated its execution and evaluated the results. This program included:

- Hydrochemical Study of the Twin Butte area by Alberta Research Council.

- Source and Ambient Air Evaluation Study for the Twin Butte area by the Kananaskis Centre for Environmental Research.

- Pincher Creek Trace Element Study by Hardy Associates (1978) Ltd.

Several analytical projects of a less extensive nature designed to determine the quality of specific aspects of soil, air and water were undertaken by:

Saskatchewan Research Council
Chemex
University of Calgary, Physics Department
University of Windsor, Chemical Engineering Department
Metro Tech Systems Ltd.
Alberta Research Council
Chemical and Geological Lab
Others

The work of the Task Force is documented in this Executive Summary, a more detailed Technical Report and three separate volumes of Technical Appendices. These documents were prepared by the Task Force Members and were then reviewed and approved by the Task Force as a whole before publication. The Task Force expresses its appreciation to Executive Suite Business Centres Ltd. for editorial and word processing assistance provided during the preparation of the several draft and final documents.

CHAPTER TWO

SURFACE WATER AND GROUNDWATER HYDROLOGY

The purpose of this aspect of the study was to determine the potential of surface water and groundwater contamination due to sour gas plant operations in the Twin Butte area.

The reconnaissance field program completed by Monenco in November 1982 at the Gulf Canada Resources Inc., Pincher Creek plant identified several toxic metals in high concentrations in wastewater and surface runoff collection ponds and high levels of sulphates in groundwater in the sulphur block area. The results of this study raised the concerns of the local residents regarding potential health

hazards related to the potential surface and groundwater contamination resulting from the plant operation.

Five potential sources of surface water and groundwater contamination were considered by the Task Force. These were:

- accidental spills of contaminants on the sites,
- seepage from process basins and surface runoff ponds,
- leachate movement from the landfill sites,
- effluent disposal,
- precipitation of gaseous emissions from the incinerator and flare stacks and sulphur dust deposition on the ground surface.

It was also recognized that organic compounds from the incinerator and flare stacks could contribute to water contamination. Rather than analyzing each water sample for hundreds of possible organic components, it was decided to conduct a survey of components leaving the plants via the air mass. Since that survey identifies that there were organic compounds of concern in the air, an additional water sampling program is being recommended.

The study area is located within the eastern flank of the Rocky Mountain Foothills. Ground surface elevations in the Twin Butte and Hill Spring area range from approximately 1500 m above sea level at the Shell Waterton Gas Plant area to approximately 1180 m above sea level at the Waterton Reservoir.

The area has a well-developed surface drainage system, represented by a number of creeks, which belong to the Waterton River drainage basin.

The climatic conditions in the Twin Butte area may be classified as humid continental. The mean annual precipitation ranges from 508 mm in the northwestern part to 815 mm in the southwestern part of the area. Potential evapotranspiration is relatively high and may be in the order of 400 mm. The mean annual temperature is approximately $4^{o}C$.

The geological conditions in the Twin Butte area are highly variable. The Quaternary deposits overlying the bedrock formations consist of glacial, alluvial, glaciofluvial and lacustrine deposits with total thicknesses ranging from less than 1 m to over 50 m.

The bedrock in the area is represented mostly by shales and sandstones representing different formations of the Cretaceous age. The structural conditions are very complex due to a number of major faults intersecting the region.

SURFACE WATER QUALITY

A number of chemical and biological surveys were conducted in the period 1971 - 1983 to assess the potential impact of the Shell and Gulf gas plant operations on surface water quality in the Twin Butte area. The results of the studies indicate some changes in the water quality of North Drywood Creek and Drywood Creek, which might be attributed to plant effluent. Other creeks in the Waterton River watershed appear not to have been affected by the plant operations.

Shell Waterton Gas Plant

A discharge of slightly brackish Shell Plant effluent with total dissolved solids ranging from 1334 to 3594 mg/L has increased the amount of dissolved matter in the North Drywood Creek to a maximum measured level of 1357 mg/L (83.02.09) below the effluent discharge point. Further downstream at the highway #6 crossing, the TDS ranged from 210 to 818 mg/L. The background level of total dissolved solids measured in the creek was 229 to 349 mg/L.

An increase in calcium, sodium, sulphate and chloride concentrations is observed immediately below the Shell Plant effluent discharge point. The concentration of these ions decreases gradually due to dilution downstream. The plant also introduces nutrients to the North Drywood Creek. Above the discharge point, concentrations of ammonia and phosphate are below the detection limits (for both compounds - 0.1 mg/L) while below the discharge point, their concentrations vary as follows:

ammonia - below detection limit to 0.3 mg/L
phosphate - 0.2 to 2.3 mg/L.

The presence of nutrients encourages algal growth in the stream water.

The increase in trace element concentrations in the North Drywood Creek is difficult to define since in many instances, concentrations of these elements in the effluent are very low. According to the available chemical analyses, an increase in the following trace

element concentrations was observed below the Shell Plant discharge point. These are: arsenic, boron, selenium, zinc, lead and nickel, with only selenium and arsenic exceeding the maximum acceptable concentrations for drinking water. Further downstream, at the Highway #6 crossing, concentrations of both selenium and arsenic were always below the maximum acceptable for drinking water.

High concentrations of arsenic in the Shell Plant effluent were traced to the gas well Waterton #42. To avoid surface water contamination in the future, formation water from the Sheet IV wells is injected into a deep disposal well.

Very small quantities of cyanide (0.05 to 0.07 mg/L) were observed in the plant effluent in the spring of 1983. The cyanide concentration rose from less than the detection limit (0.01 mg/L) upstream from the plant to 0.02 mg/L in the stream below the discharge point. This value is approximately one tenth of the maximum acceptable concentration for drinking water.

Gulf Pincher Creek Gas Plant

The study conducted by Monenco Consultants Ltd. at Gulf's Pincher Creek Gas Plant (1983) indicates the presence of brackish water in some ponds. Dominant ions are calcium, magnesium, sodium and sulphate with the last reaching concentrations in the order of 4,000 mg/L in the sulphur block runoff pond (Pond 8). The ammonia-nitrogen concentrations in Pond 8 substantially exceed background levels.

Samples taken by Monenco from the ponds for trace element analyses were not filtered. Since the tests were intended to determine levels of dissolved rather than suspended matter, the results may not be representative.

In the sulphur block runoff pond, where water is highly acidic (pH = 2.2), concentrations of all tested trace elements, with the exception of barium, substantially exceeded the background levels. Similar results were obtained from the lake located southwest of the solid waste disposal pit. Other reservoirs (Ponds 6, 7, Pond 6 weir and Pond 9) contained water with iron, manganese and chromium concentrations higher than observed in the control samples.

The highest cyanide concentrations were observed in Ponds 6 and 9 and the surface drainage channel south of the landfill area (maximum - 0.001 mg/L). Even such a low concentration appears to be slightly higher than those observed in surface water samples collected in the adjacent areas.

The hydrocarbon concentrations measured on-site are similar to those observed in the off-site water samples.

During the course of the Monenco study (1983), no water from the retention ponds was discharged to the surface drainage system. Therefore no data on water quality in the Drywood Creek below the discharge point is available.

GROUNDWATER QUALITY

The groundwater quality depends on many factors; climatic conditions, type of deposits in which groundwater is present, and circulation conditions. Since most of the wells tested in the area are relatively shallow (less than 100 m deep) it was assumed that the samples represent groundwater occurring within a zone of active water exchange. This assumption was later confirmed by the environmental isotope study. A lack of geological logs for most of the wells makes it impossible to differentiate between samples collected from Quaternary and Cretaceous deposits. Most of the wells were completed in Quaternary deposits, with only a few reaching the bedrock.

The water yielding characteristic of Quaternary sediments depends on the thickness of the deposit, hydraulic conductivity, lateral extent, terrain topography and recharge conditions. The hydraulic properties of these deposits vary from medium hydraulic conductivity silty sands and gravels to low hydraulic conductivity till and clay deposits. The presence of different types of deposits affects the groundwater recharge and circulation conditions. These variable conditions contribute to the presence of different hydrochemical types of groundwater in the study area.

The majority of groundwater samples represent the calcium-magnesium-bicarbonate type. Less common are the calcium-magnesium-sulphate, sodium-sulphate and sodium-bicarbonate-sulphate types. The total dissolved solids range from approximately 300 to 5,000 mg/L. Groundwater has a slightly alkaline character with pH varying between 7.0 to 9.6.

Groundwater with high TDS usually has high SO_4 content, which may exceed 3,500 mg/L (maximum acceptable for drinking water is 500 mg/L). Chloride concentrations in groundwaters present in the study area are very low.

Nitrate concentrations in many shallow wells and springs are very high, reaching 156 mg/L (as N). Domestic sewage and seepage from barnyards are common sources of nitrates in the groundwater in the rural areas. Other sources of nitrates may be fertilizers and industrial plant effluents. According to the information obtained from the local residents, use of fertilizers in the study area is very limited. The concentration of nitrates in the Shell Plant effluent is usually low and does not exceed 10 mg/L.

Hendry et al. (1984) determined that the high nitrates found below groundwater surface in the weathered till are the result of the oxidation of ammonium present within the tills. Nitrate concentrations in groundwater samples collected in southern Alberta may exceed 300 mg/L.

Iron and manganese are very common constituents of groundwater in the study area with maximum concentrations of 20 mg/L and 1 mg/L respectively. These values exceed maximum acceptable concentrations for drinking water, which are 0.3 mg/L for iron and 0.05 mg/L for manganese.

Other trace elements (eg. mercury, cadmium, chromium, lead, arsenic) were found in groundwater at concentrations that in general did not exceed Canadian Drinking Water Standards.

Higher concentrations of toxic metals such as lead, chromium and cadmium, were detected in groundwater samples on isolated occasions in different wells. Some of the wells were sampled several times with only one analysis indicating anomalously high concentrations of a particular element. These anomalies may be attributed either to erroneous analyses or improper sampling techniques which led to sample contamination.

The distribution of trace elements in groundwater collected in the area adjacent to the Shell and Gulf gas plants does not indicate any sign of industrial pollution.

Shell Waterton Gas Plant

The knowledge of hydrogeological conditions at the Shell Waterton gas plant is limited. Therefore, it is not possible to define the existence and extent of potential groundwater contamination zones within the plant area.

Terrain topography (largely flat areas) and the presence of permeable deposits (gravel, sand and silt) on the ground surface indicate the potential for groundwater contamination as a result of accidental spillage of chemicals or seepage from the retention ponds. Installed piezometers appear to indicate certain groundwater contamination in the plant area which is expressed by variable main ion composition, higher TDS, elevated levels of nitrate/nitrite, high iron, manganese and local chromium concentrations. These parameters are different from those observed in springs and seeps not affected by the plant operation.

A review of the available geological and hydrogeological information indicates that the groundwater flow from the majority of the Shell plant area is directed toward the North Drywood Creek Valley. Localized areas may be also drained towards the north and east of the plant. The quality of water in a spring located south of the plant in the North Drywood Creek Valley (Spring No. 1) has been affected by seepage from the sulphur block surface run-off pond. It exhibits very high sulphate concentrations (over 1,000 mg/L) and higher concentrations of main ions in comparison with other springs and seeps monitored.

Groundwater in four nests of piezometers located immediately north and east of the processing facilities and ponds at the Shell plant was contaminated with sulpholane (a chemical used in the sour gas treatment process) in concentrations up to 100 ppm. A natural water seep 1 km west of the plant reservoir contained no sulpholane.

Sulpholane is essentially non-toxic, but its use as a solubilizing agent in the plant process suggests that other, potentially more toxic compounds might enter groundwater in conjunction with it.

Only low concentrations of other organic compounds were detected in groundwater samples taken in June 1984. A more extensive set of piezometer nests should be installed to permit monitoring of groundwater at the Shell plant in future. This should make it possible to monitor sulpholane and associated compounds, and to delineate the extent of contaminated groundwater zones.

Gulf Pincher Creek Gas Plant

The Gulf Pincher Creek Gas Plant is situated in an area where a thick layer (30 to 42 m) of silty clay till of low hydraulic conductivity overlies the older sediments. In this area, movement of contaminants would be relatively slow and, in most cases, restricted to the upper water bearing zone. Higher hydraulic conductivity lenses (more silty or gravelly layers) were found throughout the till. It is believed that these layers are discontinuous and are not hydraulically connected.

The areas of groundwater contamination due to plant activities and seepage from the ponds within the Gulf property are delineated in the Monenco Reports #5 and #6. The available data indicate that the zones of contaminated water are localized within the plant boundaries. The only exception is an area located southeast of Pond 8, where higher sulphate and total dissolved solids concentrations were observed over 100 m beyond the plant limits within the upper aquifer. In the same area, a piezometer (29-1) installed within the preglacial gravel deposits underlying the till deposits (lower aquifer) indicates the presence of groundwater with raised total dissolved solids and sulphate concentrations. The origin of these anomalies should be investigated further by Gulf to determine the source of anomalous sulphate concentrations. If the anomalies in both aquifers are related to the plant operation, it would indicate that in the general area of Pond 8, a hydrogeological window exists, which allows groundwater movement from the upper aquifer through the till into the lower aquifer.

All existing data on organic chemicals in groundwater on or near the Gulf plant site were summarized in a memorandum from Monenco Consultants Ltd. to Gulf Resources Ltd., appended to the Technical Report of this Task Force (Appendix H-2).

Groundwater at the Gulf plant was severely contaminated directly beneath a waste pit used for unflared residues for many years; fortunately, this contamination is centrally located on the site. Samples taken from the site periphery or off-site had little or no contamination with organic material.

During the past exploration programs, a number of piezometers were installed in the plant area. The existing groundwater observation network will be supplemented by Gulf with additional piezometers in the future. Selected piezometers will be utilized as permanent groundwater monitoring points.

CHEMICAL WEATHERING POTENTIAL

The purpose of this laboratory experiment conducted by Dr. E. I. Wallick (Alberta Research Council) was to define the potential for release of toxic heavy metals from local till material in an SO_2 enriched atmosphere. If the release of heavy metals from till were found to occur at SO_2 concentrations much higher than those present in the vicinity of the sour gas plants, the position could be taken that given sufficient time, the metals would be leached at much lower concentrations of SO_2 in the air.

The weathering experiments were conducted on six till samples over 16 days in a control and in a variable atmosphere chamber. Only one sample showed a noticeable drop in pH (2.4) under an atmosphere containing a partial pressure of SO_2 corresponding to a concentration of 0.34 percent (3400 mg/L). This indicates a lower buffering capacity of this particular sample till. The drop in pH was associated with an increase in concentrations of trace metals. The trace metals released were not at a toxic level, as defined in "Guidelines for Canadian Drinking Water Quality", even at a pH as low as 2.4. The obtained results indicate that the release of trace metals may conceivably occur at very high concentrations of SO_2. The remaining five samples showed a decrease of pH from approximately 9 to 7. At this pH level, no increase in trace element concentrations could be observed.

Gaseous emissions from the incinerator stack are dispersed into the atmosphere, creating low concentrations of SO_2. Concentrations of SO_2 in the weathering chamber were several hundred times higher than the SO_2 concentrations observed in the air in the plant vicinity (in the order of 0.02 mg/L). Making simplifying assumptions, a one-day test at an SO_2 concentration of 34 mg/L may be considered as an equivalent to 1700 days (approximately 4.6 years) under field conditions. For higher SO_2 concentrations (3400 mg/L), a one-day test would be the equivalent of 465 years. Based on these tests, there is no reason to believe the release of SO_2 has had or will have an adverse affect on groundwater quality.

The most important observations based upon the analysis of six till samples from the Twin Butte area are that a

threshold partial pressure exists below which there is little or no reaction of SO_2 with an aqueous suspension of soil/till, and that the release of trace metals can occur only if the pH of the soil water system falls to 3.0 approximately. The threshold value of the partial pressure of SO_2 corresponds to a concentration of between 34 mg/L and 3400 mg/L for the materials studied. Increasing amounts of organic carbon, calcium, sulfate, silica, copper, lead, cadmium, cobalt, nickel, manganese, vanadium, chromium, strontium, aluminium, and zinc were released upon exposure of a shallow till sample to 0.34 percent SO_2.

CHAPTER THREE

METALS AND SULPHUR ISOTOPES IN SOIL VEGETATION & SEDIMENT

Soon after the Task Force was commissioned, reports on studies of possible metal emissions from the Gulf and Shell gas plants were released which attracted much publicity, in particular the report by Snider (1983).

The evidence in these reports was conflicting and the members of the Task Force decided that further work was necessary in order to establish whether or not significant amounts of potentially toxic air-borne metals have been deposited in the area near the gas plants during their years of operation.

In order to accomplish this objective, soil, leaf litter, grass and lake sediment samples were taken from sites beside lakes (referred to below as "lakeside samples") at various distances up to 15 km from the gas plants. These samples were analyzed for the following suite of metals: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn). Soil, litter and sediment samples were also analyzed for pH and electrical conductivity.

In addition to these measurements, garden vegetables were obtained from residents at various distances up to 15 km from the gas plants and also analyzed. These vegetables were taken in response to the suggestion that by eating home-grown vegetables, residents of the area might unwittingly be ingesting large quantities of some metals.

The soil, litter, grass, lake sediment and garden vegetable samples were also analyzed for $^{34}S:^{32}S$ ratios. In the samples analyzed, this measurement indicates the relative proportions of sour gas sulphur (rich in ^{34}S, the heavier stable isotope of sulphur) and sulphur derived from natural sources, which is richer in ^{32}S.

Bullrush samples were taken downslope from the settling ponds at both the Shell and Gulf plants and from three ponds at the Gulf plant.

Sediment samples and water from settling ponds at the Shell plant were collected and analyzed. These measurements were undertaken in keeping with the terms of reference of the Task Force, in particular the requirement to investigate the possibility of sub-surface migration of toxic substances from the gas plant sites.

AIRBORNE POLLUTION STUDIES

This section summarizes the analysis of "lakeside" samples and home-grown vegetables for metals and sulphur isotopes.

Metals in "Lakeside" Samples

The results of analyzing the grass, litter, topsoil and sediment samples from near the various lakes are given in full in the report by Hardy Associates appended to the main report (Appendix S-1).

A comparison of the results with average metal concentrations in soil and grass indicates that "lake-side" grass generally contained smaller concentrations of metals than are normally found in grass. Concentrations of metals in the corresponding soil samples were within a factor of 2 or 3, compared to those normally found in soil.

More important than the absence of any abnormally large metal concentration, for present purposes, is the absence of any trend in the results with either point of origin, or proximity to the sour gas plants. This finding refutes the suggestion that any substantial deposition of the metals analyzed for has occurred as a result of aerial transport from the sites of sour gas processing operations.

Equally, there were no trends in pH and electrical conductivity of topsoil, litter and lake sediment that might indicate contamination due to gas plant operations.

Sulphur Isotopes in "Lakeside" Samples

Results of measuring $\delta^{34}S$ values (the ratio of ^{34}S to the more common ^{32}S, expressed in parts per thousand) in elemental sulphur from the sulphur block at the Gulf plant; from untreated sour gas from the Gulf plant and from the two separate "sheets" processed by the Shell plant; and from atmospheric samples of particulate material and of air filters exposed for approximately one day downwind from the Shell plant show that windblown elemental sulphur and other forms of air-borne sulphur from the gas plants have strongly positive $\delta^{34}S$ values in the range 16-25.

In general, the values found in soil samples ranged from around zero to minus 5 in samples taken from sites near the Drywood Creek valley which connects the Shell and Gulf plants, and fell to more negative values at sites further away, with the most negative value being found at Marna Lake, 16 km northwest of the Shell plant.

Values of $\delta^{34}S$ found in grass and especially in surface litter samples were much more positive, and most lake sediment values much more negative than those for soil. The relative values for grass and for the A horizon of soil at a site may be the best indicator of sulphur deposition there due to gas plant operation.

These relative values indicate a zone of intensive ^{34}S deposition in the direction of the Drywood Creek valley at least as far east as the Waterton Reservoir, another zone in the direction of the Pincher Creek valley at least as far north as Daigle Lake, and possibly another zone in the direction of the valley of Foothill Creek as far as Rouleau Lake.

Metals in Potatoes and Carrots

The potatoes and carrots submitted by residents were also analyzed; the results indicate that eating ordinary servings of these vegetables would supply only a portion of the average daily intake of the elements normally contained in food.

There were no trends in the results when viewed in relation to the source of the samples.

The implications of these results are that there is no sign that sour gas processing operations have affected concentrations of any element analyzed for, and that the vegetables sampled would not provide a dangerously large amount of any of these elements, when included in the diet.

Sulphur Isotopes in Vegetables

The $\delta^{34}S$ values for the potatoes and carrots submitted by local residents to Mr. Bob Lyons, the District Agriculturist, generally followed the trend described above. The most positive values were observed, for the most part, at sites near the valley of Drywood Creek.

Implications of Sulphur Isotope Studies

Since any pollution by metals emitted from the gas plants would follow a similar trend to that observed for air-borne sulphur it follows that, in the absence of any discernible trend in concentrations of metals with distance and orientation of the sampling sites from the gas plants, the amounts of these metals are insignificant compared with amounts present naturally.

OTHER STUDIES

This section of the report summarizes the analysis for metals and sulphur isotopes in bullrushes, metals in the settling ponds of the Shell Waterton plant and selenium in topsoil at the Gulf Pincher Creek plant.

Metals in Bullrushes

Bullrushes downslope from the Shell plant had metal concentrations in tops and roots similar to or smaller than those found in bullrushes taken from lakes up to 15 km away. However, some bullrushes from ponds at the Gulf plant, and downslope from the Gulf plant, had high concentrations of chromium, lead and zinc relative to those in the control samples.

The results are consistent with contamination of parts of the area downslope from the settling ponds at the Gulf plant having occurred due to surface run-off. This contamination is not seen as a serious hazard, but supports the suggestion made earlier under Groundwater Quality in Chapter Two that the area south-east of the settling ponds at the Gulf plant continue to be monitored in future.

Metals in Settling Ponds at the Shell Plant

The results of analyzing nine settling ponds at the Shell plant show that sediment samples from those ponds contained concentrations of metals higher than those found in lake sediments by a factor of approximately 2 generally and, in some instances, by a factor of approximately 5.

This finding is not surprising given the function of the settling ponds. Concentrations of cadmium, mercury and zinc were similar to those reported by Monenco Ltd. in their preliminary estimate of pond sludge residues at the Gulf plant. Concentrations of chromium were much less in the Shell plant sediment than at the Gulf plant, due presumably to the absence of chromium compounds from the Shell processing treatment.

It has already been pointed out in Chapter Two of this executive summary, that there is no sign that metals from the settling ponds have leaked into groundwater in the vicinity of the Gulf and Shell plants.

Concentrations of metals in the water of the settling ponds were generally very low and mostly within acceptable quality standards for drinking water.

Tentative estimates of sludge volumes in the settling ponds at the two plants suggest that the Shell Waterton plant contains less than half the volume of sludge remaining at the Gulf Pincher Creek plant.

Selenium in Surface Soil at the Gulf Plant Site

The results of analyzing soil from three places on the Gulf site (Table IV-8) show that soil whose pH had been severely depressed by contamination with oxidized sulphur had considerably more total selenium than uncontaminated soil.

In view of this result, it seems unlikely that soil acidification caused by oxidation of wind-blown elemental sulphur would depress selenium uptake by vegetation and thereby induce selenium deficiency in grazing animals.

CHAPTER FOUR

GASEOUS AND PARTICULATE EMISSIONS

Chapter Five of the main report relates to surface migration from the Gulf Pincher Creek and Shell Waterton plants through gaseous and particulate emissions leaving the incinerator and flare stacks as well as particulate and gaseous matter carried by the wind from above the plant site to the neighbouring lands. To gain the necessary background for the study, the reports of several other studies pertinent to this phase of the work were examined to assist in the formulation of a program of work and to check on other identified matters of concern.

EMISSIONS FROM THE INCINERATOR

The report by the University of Windsor group on trace element emissions from stacks indicated that aluminum, copper, iron, titanium and zinc were lost from the plant system in amounts ranging from 1.3 to 140 g/h (grams per hour) from the incinerator stacks of the plants. Analyses of the soil and dust in the vicinity of the air blowers of the Claus unit at each plant suggest that these metals probably came from the soil and dust picked up by the winds and carried through the reaction system to the incinerator. The amounts of these elements likely to be ingested from the air by people living in the area are reported to be negligibly small compared with the estimated daily intake from food sources.

In view of the relatively long reaction time, the excess of oxygen and the high temperatures throughout the incinerator stacks, it was considered that any residual organic compounds in the waste gases sent to the incinerator would be combusted completely, forming carbon dioxide and water. It was learned from Shell that through its own investigations the presence of carbonyl sulfide at concentrations of a few parts per million were found in the incinerator stack effluent along with the residual sulfur dioxide from the Claus process. It is possible that this carbonyl sulfide was responsible in part for the odour sometimes detected downwind from the plant. In view of the work done by the Windsor Group and Shell on components being emitted by the incinerator stack, the Task Force decided not to pursue these studies further.

EMISSIONS FROM FLARE STACKS

Reports by M. T. Strosher of the Kananaskis Centre for Environmental Research and by Sciex indicated the presence of trace organic compounds in the air downwind from the plant. For this reason, additional studies were made using the "Tenax" adsorbent technique to collect heavier components in the air so that they could be later analyzed by a GC/MS instrument at the Kananaskis Centre. At the same time analyses were made with a trace sulphur gas analyzer. Samples were taken of the air at various points downwind and upwind from the plant as well as of the gas leaving the flare stack of plant No. 2 while gases from various points in the process were being vented to this flare. The results of the GC/MS analyses done downwind from the plant show a remarkable correspondence in the compounds identified when compared with samples obtained from the flare. The presence in the ambient air of compounds such as phenol and styrene which are not present in the raw gas is considered good evidence that the organic components detected result from incomplete combustion in the flare. This incomplete combustion will contribute to the odour problem downwind due to the presence of unburned hydrogen sulphide and other sulphur containing compounds in the effluent.

The correspondence between the compounds detected in the air and those present in condensate suggests that gas being flared contains volatile components of condensate. Condensate for the most part should be trapped in the "knock out" drum immediately upstream from the flare stacks. Gases being flared, however, on passage through the "knock out" drum will carry some of these volatile components to the flare.

AMBIENT AIR QUALITY

Several compounds identified in the samples collected from the air downwind from the plant are known to be toxic and at least one such compound, benzene, is a known carcinogen (benzene and several of the toxic materials are components of gasoline). Assuming incomplete combustion under adverse flaring and dispersion conditions, the concentrations of toxic materials such as sulphur dioxide, hydrogen sulphide, benzene and phenol may increase in the atmosphere for varying periods of time, depending on weather conditions, wind speed and direction during the flaring, and the material being flared. Whether the concentrations could increase sufficiently to cause problems for certain sensitive people is not known.

While threshold limit values have been set for these substances when present in a workroom environment, safe levels for the open air have not been set. Judging by the quantitative estimates made by the Kananaskis Centre for Environmental Research in a survey of the ambient air in the vicinity of the two plants in 1981, none of the components detected was found to be at concentrations considered serious to health when judged by workplace standards. However, the residents of the area may be subjected to the emissions for longer periods than industrial workers in the workplace. Some members of the residential population also may be in a much poorer state of health than industrial workers or may be more delicate as are children and hence susceptible to the effects of toxic materials at considerably lower concentrations.

The effect of sulphur dioxide alone in the atmosphere at levels between 0.25 and 0.40 ppm has recently been reported to cause increases in airway resistance of some asthmatics undergoing exercise for periods of 5 to 10 minutes. The effects of traces of sulphur dioxide and hydrogen sulphide in combination with the traces of organic compounds found present in the air might be more severe than those of the individual compounds in isolation. Suitable well-controlled clinical tests of sensitive people in the area might possibly establish whether or not the effluents leaving the incinerator flare stacks are in any way responsible for some of the health problems about which some of the residents complain.

Based on the analysis of the air downwind from the Shell plant and on analyses of the combustion gases from the flare, there is sufficient evidence to recommend that the operation of the flare stacks be reviewed. It is further recommended that efforts be made to ensure that combustion of the waste gases sent to the flare is as complete as is technically feasible. Efforts should be made to prevent condensate from accumulating in the knock-out drum upstream from the flare.

CHAPTER FIVE

CONCLUSIONS

This chapter summarizes the main conclusions agreed to by the Task Force regarding air, soil and water quality in the Twin Butte area.

GENERAL CONCLUSIONS

In reviewing the overall impact of air, soil and water quality in the Twin Butte area, the Task Force has concluded that:

1. Based on the analytical evidence available, (Monenco Report) toxic materials are present in the ponds, in landfills and in areas actively used during the Gulf plant operations. The Task Force study indicates that, with minor exceptions, these substances are contained within the boundaries of this plant site.

2. Preliminary reconnaissance conducted by the Task Force at the Shell plant site identified the presence of sulpholane and a compound of formula $C_7H_{11}NO_3$ in the groundwater. Sludges in the tested ponds did not contain substantial quantities of trace metals. No soil survey at this plant was conducted.

3. No evidence was found that heavy metals or toxic substances in substantive quantity, originating from gas processing, have migrated from the plant sites. The exceptions to this statement were:
   - Mercury levels at piezometer (29-1) at the Gulf Pincher Creek plant were observed to be slightly higher than background levels.
   - Arsenic levels exceeding drinking water standards were identified in early 1983 at the discharge point from the Shell Waterton plant into the Drywood Creek.

SURFACE WATER AND GROUNDWATER HYDROLOGY

The impact of the Shell Waterton and Gulf Pincher Creek gas plants on water quality in the Twin Butte area have been reviewed thoroughly. The Task Force has concluded that:

1. The quality of effluent from the two plants generally complied with the Process Effluent Standards established by Alberta Environment. Occasional contraventions of these standards were observed in the past. Effluent from the Shell Waterton Gas Plant causes an increase in total

dissolved solids, main ions, nutrients and some trace element concentrations in the North Drywood Creek and Drywood Creek. The Gulf Pincher Creek Gas Plant has ceased operation; however, it is reasonable to conclude that, in the past, effluent discharge from the Gulf plant had similar downstream effects to those observed at the Shell plant.

With the exception of North Drywood Creek and Drywood Creek, no other creeks or lakes in the area have water quality distinctly affected by the Shell and Gulf plant operations.

2. The environmental isotope studies indicate that the surface water system is hydraulically continuous with the shallow groundwater system and that recharge is rapid in geological terms. Available results indicate that there is no evidence that groundwater quality is affected by SO_2 and H_2S emitted from the gas plants.

3. Groundwater quality in the wells located in the areas adjacent to the Shell and Gulf plants does not indicate the presence of anomalies which could be attributed to industrial pollution. The only exceptions to this statement are the anomalously high values of total dissolved solids and sulphates in the area extending SE of Gulf's Pond 8 and in the spring water below the Shell plant in the North Drywood Creek Valley.

4. Localized zones of groundwater contamination are present at the Shell Waterton and Gulf Pincher Creek plants. High total dissolved solids and sulphate concentrations are prime indications of groundwater contamination. At the Gulf plant, anomalous concentrations of trace elements and organic compounds, which could be attributed to the plant operation, were detected. Sulpholane, an essentially non-toxic chemical used in sour gas processing, was found in concentrations up to 100 ppm in groundwater at the Shell Waterton plant.

5. The most important observations based upon the geochemical weathering tests of six till samples from the Twin Butte area are:
   a) that a threshold partial pressure exists below which there is little or no reaction of SO_2 with an aqueous suspension of soil/till, and
   b) that the release of trace metals can occur only if the pH of the soil-water system falls below a pH value of 3.0 approximately. The threshold value of the partial pressure of SO_2 corresponds to a concentration between 34 mg/L and 3400 mg/L for the materials studied. Increasing amounts of organic carbon, calcium, sulfate, silica, copper, lead, cadmium, cobalt, nickel, manganese, vanadium, chromium, strontium, aluminium, and zinc were released upon exposure of a shallow till sample to 3400 mg/L of sulphur dioxide. The trace metals released were not at toxic levels, even at a pH as low as 2.4.

ANALYSIS OF SOIL AND VEGETATION

The Task Force has reviewed the data and concludes that:

1. Sulphur, presumably as SO_2, has been air borne in the direction of a) the Drywood Creek valley at least as far as the Waterton reservoir, b) the Pincher Creek valley as far as Daigle Lake and possibly c) the Foothill Creek valley as far as Rouleau Lake.

2. There has been no detectable increase in acidity or electrical conductivity of soil, litter and lake sediment in these areas, concomitant with the readily detectable increase in ^{34}S which has resulted from operation of the gas plants.

3. Equally, there has been no detectable, concomitant increase in concentrations of metals in soil, vegetation or lake sediment in these areas.

4. There was no indication of any increase in concentrations of metals in potatoes and carrots grown in 1983 in the study area, as a result of gas plant operations. The vegetables obtained were safe to eat.

5. There were indications of contamination with chromium, lead and zinc in bullrushes downslope from settling ponds at the Gulf Pincher Creek plant, possibly because of surface run-off.

GASEOUS AND PARTICULATE EMISSIONS

The Task Force has reviewed the data and concludes that:

1. The organic compounds detected in trace amounts in the ambient air were a result of flare stack emissions.

2. Gases directed to the flare stack during the tests contacted condensate, a volatile liquid fraction produced from the raw gas, which was trapped in the knock-out drum immediately upstream from the flare.

3. Condensate may be carried into the flare when gases from various points in the plants are flared. Combustion of this condensate was incomplete, under the conditions of the tests undertaken, giving rise to the presence of the organic compounds detected in the ambient air downwind from the plant.

4. The trace element emissions from the incinerator stack detected by the University of Windsor Group probably came from the soil and dust picked up by the wind and then carried through the reaction system.

5. The Shell plant finds it necessary to add sweet gas to sour gas when the latter is being flared to achieve greater thermal lift and to decrease concentrations of sulphur dioxide at ground level to values less than the standards set for ambient air quality. It is therefore concluded that when flaring

occurs, the sulphur dioxide levels downwind from the flare stack will tend to approach the upper limits of the standard. Insufficient dilution of the sour gas with sweet gas, coupled with adverse dispersion conditions, could cause ambient sulphur dioxide levels to exceed the standard for short periods.

CHAPTER SIX

RECOMMENDATIONS

This chapter summarizes the recommendations which have been made following detailed review of findings and conclusions regarding air, soil and water quality in the Twin Butte area.

SURFACE WATER AND GROUNDWATER HYDROLOGY

The Task Force recommends that:

1. A further survey of groundwater and surface water should be conducted to determine the presence and concentrations of organic compounds near the Shell Waterton plant. This recommendation follows from the detection of sulpholane in shallow groundwater on the

Shell plant site, and also accommodates the possibility of air-borne contamination of surface water. Groundwater samples should be subjected to a standard fish toxicity test.

2. The monitoring of surface water, spring and observation wells at the Shell Waterton plant should be continued. Additional piezometer nests should be added in the areas of Basin A, Plant #2 Slurry pond and Basin K. A detailed survey of the solid waste disposal sites should be conducted and an appropriate groundwater monitoring system established.

3. The reclamation program developed by Gulf should be implemented and progress of the work monitored by the owner and by government agencies. Since the Pincher Creek plant was the first major sour gas plant built and the first to be closed in Alberta, the experience gained in the site reclamation should be used to establish appropriate guidelines for operating and decommissioning similar plants. Additional piezometers should be installed and isotope studies conducted to define the origin of the hydrochemical anomalies SE of Pond 8 in the upper and lower aquifers. Piezometer 29-1 should be resampled and mercury concentrations in the groundwater confirmed. Groundwater samples should also be monitored for contamination by organic compounds.

4. Detailed hydrological and hydrogeological studies (including application of environmental isotopes) should be conducted, prior to any new sour gas plant construction. This would provide hydrochemical baseline data, which may be required in the future for environmental impact assessments.

5. Procedures for water sampling, preservation and transportation to be used in all hydrochemical studies should be established. Analytical methods for different ions or compounds should be recommended. Present use of methods with different levels of accuracy make evaluation and comparison of the results very difficult.

6. The results of the artificial weathering tests in the SO_2 atmosphere indicate great potential for this method in future studies related to sour gas plant operations. Further studies should be conducted to define the sensitivity of different soils in Alberta to sulphur loading and release of trace elements. This study should also include an evaluation of the potential impact on groundwater quality of the effects of deposition of sulphur dust on the ground surface.

ANALYSIS OF SOIL, VEGETATION AND SEDIMENT

The Task Force recommends that:

1. After an appropriate time interval (5 years?) measurements of $\delta^{34}S$ values in soils, vegetation and lake sediments should be repeated to establish whether an equilibrium has been reached or whether $\delta^{34}S$ values are still increasing to more positive levels. This may indicate whether potentially damaging effects of airborne sulphur deposition have reached a plateau. A more detailed

sampling would also confirm whether this airborne sulphur actually follows the valleys of the Drywood, Pincher and Foothill Creeks.

GASEOUS AND PARTICULATE EMISSIONS

The Task Force recommends that:

1. The placement, design and operation of the flare stacks should be reviewed and efforts made to ensure the most complete combustion, that is technically feasible, of the waste gases sent to flare stacks.

2. The condensate trapped in the knock-out drum immediately upstream from the flare stack should be kept at a minimum level so that gases being flared carry as little condensate as possible to the flare.

3. Plant operating procedures should be reviewed with the objective of eliminating the need for, or reducing the extent of, flaring within technically feasible limits.

4. In addition to monitoring the ambient air for sulphur dioxide and hydrogen sulphide, analyses should be made when flaring is taking place to determine whether the concentrations of organic compounds in the ambient air downwind from the plant reach levels which might be considered hazardous.

5. Future studies of the effects on animal health of compounds added to inhaled air should include the organic compounds found in ambient air near the Shell plant as well as sulphur compounds such as SO_2, H_2S, CS_2 and COS.

GENERAL RECOMMENDATION

The Task Force recommends that:

1. The operators of these and other sour gas plants should continue to maintain a close liaison with residents of local communities through such things as joint committees, newsletters, etc., to avoid misunderstanding and animosity that compromise efforts to achieve an objective appraisal of the effects of sour gas processing.